Hydrothermal Synthesis and Characterization of a Novel One-Dimensional Titanium Glycolate Complex Single Crystal: $Ti(OCH_2CH_2O)_2$

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Single crystals of a novel titanium glycolate complex, $Ti(OCH_2CH_2O)_2$, have been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, IR spectroscopy, thermal analysis (TG-DTA), and scanning electron microscopy (SEM). The titanium glycolate complex crystallizes in the monoclinic space group $C2/c$ (no. 15), with unit cell parameters of $a = 15.204(9)$ Å, $b = 7.568(2)$ Å, $c = 5.816(6)$ Å, $\beta = 110.87(6)°$, $Z = 4$, $R = 0.036$, and $R_w = 0.033$ for 598 reflections ($I > 3\sigma(I)$) and 43 variables. The structure is described as parallel chains built up from edge-sharing $Ti^{4+}O_6$ octahedra. The six oxygen atoms are offered by four ethylene glycolate ligands. Each ethylene glycolate ligand bridges two titanium atoms with one of its oxygen atoms, and the other is terminal.

Introduction

Considerable attention has been focused on the investigation of novel metal alkoxides in the past 2 decades, because of their remarkable ability as precursors for electroceramic materials.[1] The sol−gel technique, based on the hydrolytic condensation of precursors, is a low-temperature method for conversion of metal alkoxides to metal oxides.[2−4] Moreover, by use of this technique, the conversion can be controlled on the molecular level. It is always the fact that the resulting materials will retain some structural features of their synthetic precursors in low-temperature reactions. Apparently, the synthesis of new metal alkoxides possessing unique structures and properties is of great significance for the investigation of sol−gel processes as well as the evolution of metal alkoxide chemistry. However, some distinct disadvantages of metal alkoxides make it difficult to study their structures and properties thoroughly, such as the extreme moisture sensitivity, and the tendency to form mixtures of structurally complex species upon hydrolysis.[1] As a result, the preparation of most metal alkoxides is relatively complicated.

Hydrothermal chemistry has made a success of the synthesis of almost all kinds of recently important materials.[5−8] Above all, the hydrothermal technique exhibits outstanding advantages in the preparation of single crystals.

Different from most crystalline titanium alkoxides, which are generally low polymeric 0-dimensional molecular,[9−13] $Ti(OCH_2CH_2O)_2$ is a novel crystalline complex with infinite one-dimensional chains. It exhibits outstanding high stability not only in alcohol but also in water.

In the research here, we describe the successful hydrothermal synthesis and the crystal structure of $Ti(OCH_2CH_2O)_2$, and its evolution upon calcination at various temperatures.

Experimental Section

Synthesis. The crystallization of the product was carried out by using the hydrothermal method. A mixture of tetraethyl orthotitanate, *n*-butylamine, and ethylene glycol in the molar ratio 1.0:1.0:20.0, $Ti(OC_2H_5)_4$:$CH_3(CH_2)_3NH_2$:$HOCH_2CH_2OH$ was stirred for 1 h, then was put into a Teflon-lined stainless steel autoclave, and was heated at 160−180 °C for 5 days under autogenous pressures. The product was filtered and washed with distilled water and ethanol and then was dried at ambient conditions. The large transparent needle-like crystals up to several millimeters in length were obtained by this preparation.

Infrared Spectroscopy. Infrared absorption spectra (IR) were recorded on a JASCO FT/IR-410 spectrometer using transparent KBr pellets: 1−2 mg of the sample was crushed and mixed with 300 mg of KBr.

Thermal Analysis. Thermogravimetric and differential thermal analyses (TG, DTA) were carried out in a Rigaku

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(1) Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxide*; Academic Press: New York, 1978.
(2) Goel, S. C.; Kramer, K. S.; Gibbons, P. C.; Buhor, W. E. *Inorg. Chem.* **1989**, *28*, 3619.
(3) Matchett, M. A.; Chiang, M. Y.; Buhro, W. E. *Inorg. Chem.* **1990**, *29*, 358.
(4) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science*; Academic Press: San Diego, CA, 1990.
(5) Chen, C. Y.; Xiao, S. Q.; Davis, M. E. *Microporous Mater.* **1995**, *4*, 1.
(6) Feng, S.; Greenblatt, M. *Chem. Mater.* **1992**, *4*, 462.
(7) Feng, S.; Greenblatt, M. *Chem. Mater.* **1993**, *5*, 1277.
(8) Wang, D.; Yu, R.; Feng, S.; et al. *Chem. J. Chin. Univ.* **1998**, *19*, 165.
(9) Wright, B. A.; Williams, D. A. *Acta Crystallogr., Sect. B* **1968**, *24*, 1107.
(10) Ibers, J. A. *Nature* **1963**, *197*, 686.
(11) Witters, R. D.; Caughlan, C. N. *Nature* **1965**, *205*, 1312.
(12) Hampden-Smith, M. J.; Williams, D. S.; Rheingold, A. L. *Inorg. Chem.* **1990**, *29*, 4076.
(13) Day, W.; Eberspacher, T. A.; Klemperer, W. G.; Park, W. *J. Am. Chem. Soc.* **1993**, *115*, 8469.

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Table 1. Summary of Crystallographic Data for the Structures of $Ti(OCH_2CH_2O)_2$

formula	$TiO_4C_4H_8$
formula weight	167.98
crystal system	monoclinic
Z	4
space group	*C*2/*c* (no. 15)[a]
lattice parameters	$a = 15.204(9)$ Å
	$b = 7.568(2)$ Å
	$c = 5.816(6)$ Å
	$\beta = 110.87(6)°$
volume	625.3(8) Å^3
density	1.784 g/cm^3
temperature	23 °C
radiation	Mo Kα ($\lambda = 0.71069$ Å) graphite monochromated
no. of observations after averaging ($I > 3.00\sigma(I)$)	598
residuals: R; R_w	0.036; 0.033
goodness-of-fit indicator	1.60
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\| = 0.036$	
$R_w = \sqrt{\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2} = 0.033$	

[a] From the extinction rule, space groups *Cc* and *C*2/*c* are deduced. In the course of structural analysis the latter space group was found to give lower R factor than the former ($R = 0.047$, $R_w = 0.049$, GOF = 0.6). Therefore, the space group *C*2/*c* was chosen.

Table 2. Atomic Coordinates for $Ti(OCH_2CH_2O)_2$

atom	site	*x*	*y*	*z*	B_{eq}[a]
Ti	4*e*	1/2	0.09912(8)	3/4	2.05(1)
O(1)	8*f*	0.4402(1)	0.0919(2)	0.3824(2)	2.75(3)
O(2)	8*f*	0.4018(1)	0.2547(3)	0.6952(3)	3.95(4)
C(1)	8*f*	0.3620(2)	0.3335(4)	0.4610(5)	3.86(6)
C(2)	8*f*	0.3589(2)	0.1975(4)	0.2718(5)	3.49(6)

[a] $B_{eq} = 8/3\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos\gamma + 2U_{13}aa^*cc^* \cos\beta + 2U_{23}bb^*cc^* \cos\alpha)$.

Thermoflex TAS 200 thermal analysis system with a heating rate of 5 °C/min over a 20−1000 °C temperature range.

X-ray Powder Diffraction. X-ray powder diffraction (XRD) patterns were taken on a RINT 1200 Rigaku X-ray diffractometer, using Ni-filtered Cu Kα radiation. XRD patterns at high temperatures were measured up to 1000 °C in air.

X-ray Structure Determination. A transparent needle-like crystal was mounted on a glass fiber. Single-crystal X-ray diffraction data were collected by using a Rigaku AFC-7R four-circle diffractometer with graphite monochromated Mo Kα radiation.

The intensities of three representative reflections were measured after every 500 reflections. An empirical absorption correction based on azimuthal scans of several reflections was applied which resulted in transmission factors ranging from 0.88 to 1.00. The data were also corrected for Lorentz and polarization effects.

The crystal structure was solved by the heavy-atom method and expanded by Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were geometrically placed but not refined. All calculations were performed using the TEXSAN crystallographic software package. Further details of relevant crystal data are summarized in Table 1. The coordinates and anisotropic temperature factors are given in Table 2, and selected bond lengths and angles are shown in Table 3.

Results and Discussion

Synthesis. To avoid hydrolysis of products, the traditional preparations of most metal alkoxides are usually carried out under inert an atmosphere or in vacuo, and the products must be kept in the glass capillaries.[1] In our research, the hydrothermal method was employed, and the crystallization of the product took advantage of the closed system and autogenous pressure, which are the characteristics of hydrothermal synthesis. Under these conditions, single crystals of a novel titanium glycolate, $Ti(OCH_2CH_2O)_2$, with a unique infinite chain structure was obtained. The compound is a moisture-stable material.

Table 3. Selected Bond Lengths (Å) and Angles (deg)

Ti−Ti	3.2724(6)	O(1)−Ti-O(1A)	176.9(1)
Ti−O(1)	2.004(1) ×2	O(1)−Ti-O(1B)	70.47(7)
Ti−O(1)	2.003(2) ×2	O(1)−Ti-O(1C)	107.15(6)
Ti−O(2)	1.837(2) ×2	O(1)−Ti-O(2)	78.49(7)
O(1)−O(1B)	2.311(3)	O(1B)-Ti−O(1A)	107.15(6)
O(1)−O(1C)	3.224(1)	O(1B)-Ti−O(1C)	87.6(1)
O(1C)-O(1B)	2.771(3)	O(1B)-Ti−O(2A)	94.41(9)
O(1)−C(2)	1.419(3)	O(1C)-Ti−O(1A)	70.47(7)
O(2)−C(1)	1.411(3)	O(1C)-Ti−O(2A)	148.00(7)
C(1)−C(2)	1.495(4)	O(2)−Ti-O(2A)	100.3(1)
		O(2)−Ti-O(1B)	148.00(7)
		O(2)−Ti-O(1C)	94.41(9)
		Ti−O(1)−C(2)	117.4(1)
		Ti−O(2)−C(1)	118.7(2)
		O(2)−C(1)-C(2)	108.1(2)
		O(1)−C(2)-C(1)	105.0(2)

In the synthesis of the title compound, ethylene glycol was used as a solvent as well as a reactant. The investigation of the synthetic processes indicated that the alkalinity of the reaction mixture was the most important factor, which influenced the crystallization of the product essentially. The appropriate molar ratio of $CH_3(CH_2)_3NH_2$ to $Ti(OC_2H_5)_4$ is 1:1 for the synthesis. If the amount of *n*-butylamine was too large (*n*-$BuNH_2$/Ti = 2/1), no crystalline product could be obtained. When the ratio of $CH_3(CH_2)_3NH_2$ to $Ti(OC_2H_5)_4$ was less than 1:1, the rate of reaction and the crystallinity of the product were very low. The product could not be crystallized when some quaternary ammonium salts, $(C_2H_5)_4NBr$ and $(C_3H_7)_4NBr$), and a strong base such as LiOH were employed instead of $CH_3(CH_2)_3NH_2$. Recently, a number of reports have described the syntheses and structures of anionic titanium alkoxides, including $[NH_4]_2Ti(cat)_3$,[14] $Na_2Ti(OCH_2CH_2O)_3 \cdot 4C_2H_6O_2$, and $K_2Ti(OCH_2CH_2O)_3 \cdot 2.5C_2H_6O_2$.[15] In their syntheses, the alkalinity also played an important role.

Structure. The combination of titanium tetraalkoxides with bidentate chelate alkoxides such as glycol[16] or 2-methylpentane-2,4-diol[17] have been studied in the literature. According to the ratio of titanium to the chelate diol, the neutral compounds were characterized by various complex geometry, but none of their structures could be clearly determined.

The structure of $Ti(OCH_2CH_2O)_2$ was solved in the C-centered monoclinic space group *C*2/*c* and consists of one-dimensional chains of edge-sharing $Ti^{4+}O_6$ octahedra along the *c*-axis as shown in Figures 1 and 2. The packing arrangement of $Ti(OCH_2CH_2O)_2$, seen in Figure 3, shows that the parallel chains align such that each chain has six neighbors, with no direct linkage between adjacent chains. The chains are held together by a van der Waals interaction, thereby forming an extended structural array. There are two oxygen atoms in bridg-

(14) Borgias, B. A.; Cooper, S. R.; Koh, Y. B.; Raymond, K. N. *Inorg. Chem.* **1984**, *23*, 1009.
(15) Gainsford, G. J.; Kemmitt, T.; Lensink, C.; Milestone, N. B. *Inorg. Chem.* **1995**, *34*, 746.
(16) Reeves, R. E.; Mazzenom, L. W. J. *J. Am. Chem. Soc.* **1954**, *76*, 2533.
(17) Yamamoto, A.; Kawbara, S. *J. Am. Chem. Soc.* **1959**, *81*, 2663.

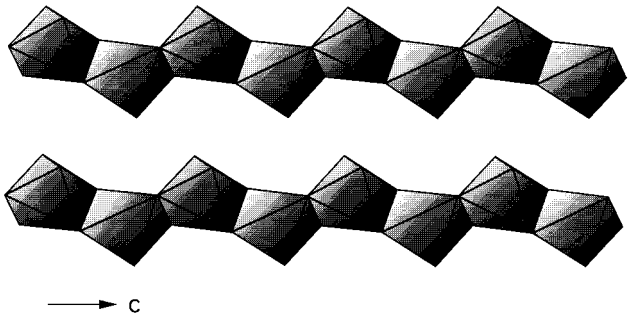

Figure 1. Polyhedral view of the one-dimensional chains of $Ti(OCH_2CH_2O)_2$ along the *c* axis.

ing positions between two adjacent octahedra, denoted O(1) and O(1B) in Figure 2. In the structure, each ethylene glycolate ligand links two titanium atoms such that one oxygen atom of the ligand is bridging, O(1), and the other is terminal, O(2).

All the titanium atoms have an equivalent environment, a coordination number of 6, completed as follows: two bridging oxygen atoms shared by Ti and Ti*, another two bridging oxygen atoms shared by Ti and Ti**, and two terminal oxygen atoms.

In the titanium octahedra, the bond lengths Ti−O vary from 1.837(2) to 2.004(1) Å (average 1.948 Å). The Ti−O bond to the terminal O(2) is short (1.837(2) Å) and the Ti−O(2)−C(1) angle is 118.7(2)°. In contrast, the Ti−O bonds of bridging O(1) are relatively long (2.004(1) and 2.003(2) Å), and the Ti−O(1)−C(2) angle has a slightly smaller value (117.4(1)°) than the Ti−O(2)−C(1) angle. In addition, because of the edge-sharing of the octahedra, the Ti−O distances to the bridging oxygen atoms are elongated by about 0.17 Å when compared with the Ti−O(2) distance of 1.837(2) Å, and the bond angle between the bridging oxygen atoms is considerably small. As a consequence, the TiO_6 is considerably distorted from ideal octahedral coordination. The Ti···Ti* distance is 3.2724(6) Å as compared with 3.326(1) Å found in the structure of dimeric $[Ti(DTBC)_2(HDTBC)]_2$,[14] and 2.994 Å found in anatase for edge-sharing TiO_6 octahedra along the *c* axis.

As for the gaseous ethylene glycol molecule, the bond lengths for C−C and C−O are 1.52 ± 0.02 and 1.43 ± 0.02 Å, respectively, and the C−C−O angle is 109.5°.[18] In the title compound, when the ethylene glycolate ligand is combined with the titanium atom as a bidentate chelate, the bond length C(1)−C(2) gets a little shorter (1.495(4) Å) than that of the ethylene glycol molecule, and the C−C−O angles for C(2)−C(1)−O(2) and C(1)−C(2)−O(1) become smaller in varying degrees (108.1(2)° and 105.0(2)°, respectively). Moreover, the angle between C(2)−C(1)−O(2) and C(1)−C(2)−O(1) planes decreases from 74° of ethylene glycol to 34.4°. The C−O bond distances for C(2)−O(1) (1.419(3) Å) and C(1)−O(2) (1.411(3) Å) are in good agreement with those of ethylene glycol.

The stability of polytitanates $[Ti_xO_y][OR]_{4x-2y}$ was discussed in terms of the degree of condensation y/x.[19] The steric repulsion between alkoxide ligands was also

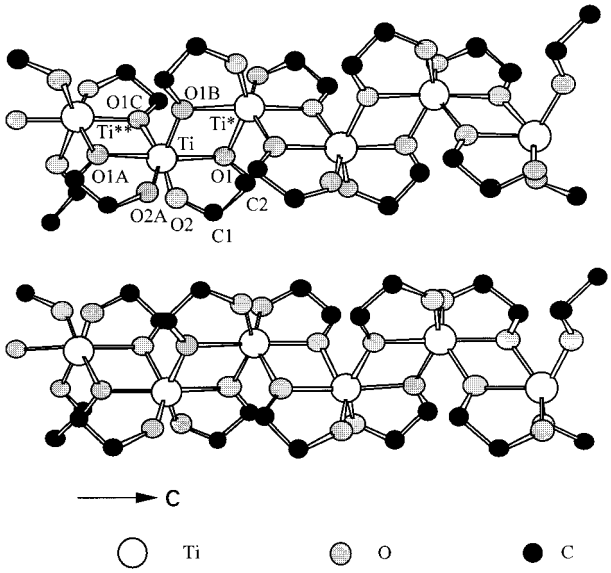

Figure 2. View of the one-dimensional chains of $Ti(OCH_2CH_2O)_2$ along the *c* axis.

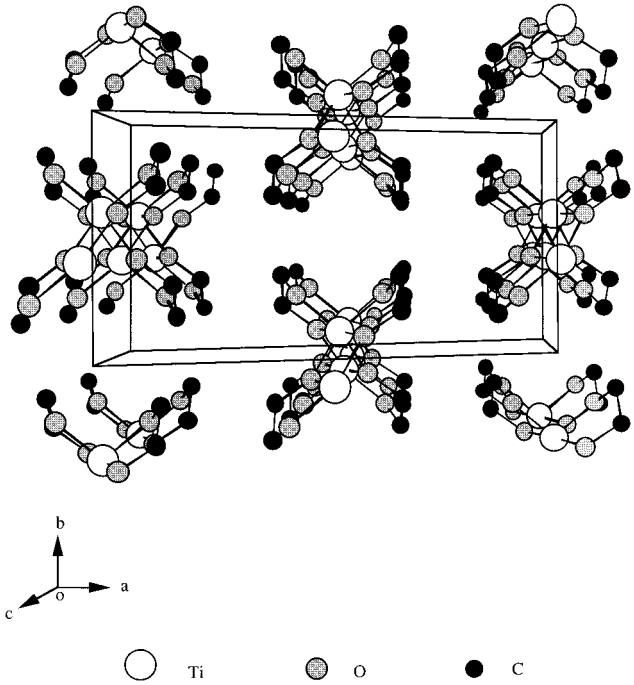

Figure 3. View of $Ti(OCH_2CH_2O)_2$ with the unit cell outlined showing the pack along the *c* axis.

pointed out to destabilize titanium alkoxide hydrolysis products.[19] The degree of condensation $y/x = 0$ for the compound obtained here implies that the compound is very unstable. However, as each ethylene glycolate ligand locates apart from others by more than the van der Waals diameter of the methyl group in this compound, no steric repulsion is conceivable. Furthermore, an infinite TiO_2 chain is the structure unit of the compound, contrary to molecular units of polytitanates. Therefore, we cannot evaluate the stability of $Ti(OCH_2CH_2O)_2$ only by the degree of condensation.

Infrared Spectroscopy. The IR spectrum of the title compound dispersed in KBr is shown in Figure 4. The bands located at 2927 and 2855 cm^{-1} are assigned to the stretching vibrations of ν(C−H). This is consistent

(18) *Tables of Interatomic Distances and Configuration in Molecules and Ions*; The Chemical Society Burlington House: London, W.1, 1958.
(19) Day, V. W.; Eberspacher, T. A.; Chen, Y. W.; Hao, J.; Klemperer, W. G. *Inorg. Chem. Acta* **1995**, *229*, 391.

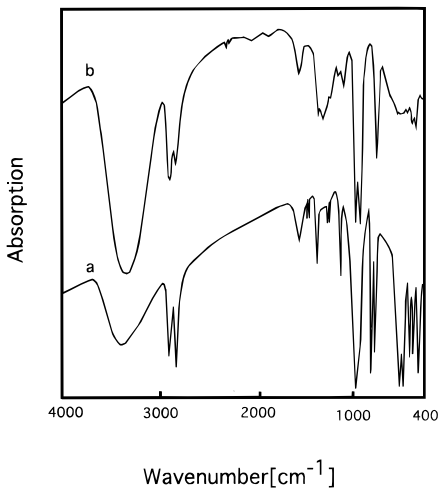

Figure 4. IR spectra of (a) $Ti(OCH_2CH_2O)_2$ and (b) $HOCH_2$-CH_2OH.

with the symmetric and antisymmetric C−H stretching bands of ethylene glycol, roughly.

The Ti−O stretching frequency for $Ti(OiPr)_4$ has previously been assigned to a band at 619 cm^{-1} and is characteristic for titanium alkoxides.[12] It has been mentioned recently that the bands located around 1100 and 675−550 cm^{-1} were characterized for the presence of Al−O−C linkage in a barium aluminate glycolate[20] and Ti−O−C linkage in a barium titanium glycolate.[21] Other research indicated that the C−O−Ti bands characteristic of butoxy groups linked to titanium are located at 1035, 1085, and 1135 cm^{-1}.[22] The presence of bands at 1086 and 1042 cm^{-1} were characterized as a C−C−O stretching vibration for ethylene glycol. However, in the crystalline phase, these two absorption bands disappeared, indicating that H−O−C bonds have been replaced by Ti−O−C bonds. Therefore, three bands at 1124, 1057, 1030 cm^{-1}, and two bands at 635 and 595 cm^{-1} can be assigned to C−O−Ti, characteristic of ethylene glycolate ligands linked to titanium. The bands occurring at 635 and 595 cm^{-1} are assigned to the ν(Ti−O) stretching frequency for the Ti−O(2) and Ti−O(1) band, respectively, according to their different bond lengths. The bands at 536, 498, and 442 cm^{-1} are assigned to the Ti−O−Ti stretching and bending vibrations. Some of the bands at around 1400 cm^{-1} are diagnostic of ethylene glycolate ligands in the gauche conformation.

Thermal Analysis. To investigate the thermal properties of titanium glycolate $Ti(OCH_2CH_2O)_2$, TG-DTA analyses were carried out in air and the results are shown in Figure 5. The DTA curve shows an exothermic effect occurring at ca. 338 °C. This is in good agreement with the TG results. The TG curve has one step ranging from 310 to 350 °C, corresponding to the weight loss of ca. 50%, which is consistent with the calculated value (53%) for all organic groups separating themselves from the framework. Upon oxidation of the organic moiety in the temperature range mentioned above, the compound changed to an amorphous state as shown by the XRD pattern of Figure 6 d. With an increase in the calcination temperature, the XRD pattern of anatase became discernible at 400 °C and that of rutile was observed above 650 °C, coexisting with anatase. A single phase of rutile was obtained at 1000 °C. The transformations from the amorphous to anatase and from anatase to rutile were so gradual that no clear thermal effect was seen in DTA curves.

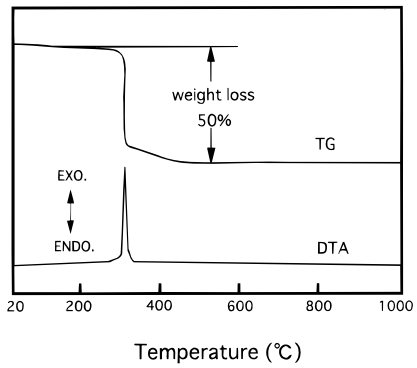

Figure 5. TG-DTA curves of $Ti(OCH_2CH_2O)_2$.

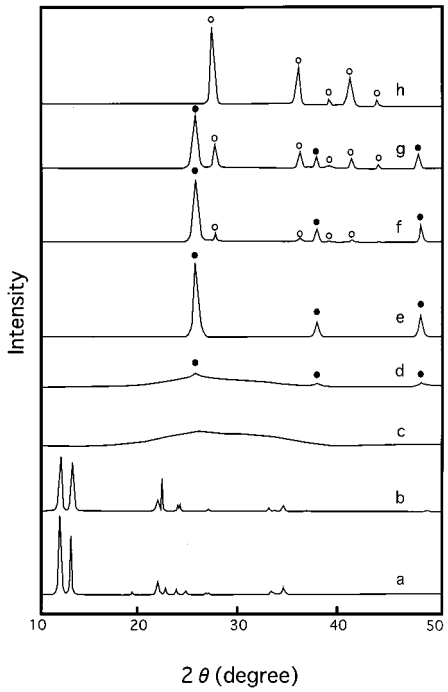

Figure 6. XRD patterns of the product at different temperatures: (a) 25 °C, $Ti(OCH_2CH_2O)_2$; (b) 200 °C, amorphorous; (c) 300 °C; amorphous; (d) 400 °C, appearance of anatase (shown by filed circles); (e) 500 °C, anatase; (f) 650 °C, appearance of rutile (shown by open circles); (g) 700 °C, mixed phase of anatase and rutile; (h) 1000 °C, rutile.

There is a particular phenomenon which attracted our attention. Upon calcination at appropriate temperatures, $Ti(OCH_2CH_2O)_2$ transformed into anatase and rutile in sequence. Although the compositions as well as the structures of these two types of titanium dioxides are very different from the as-synthesized product, both of them hold the shape of the as-synthesized titanium glycolate $Ti(OCH_2CH_2O)_2$ crystal. The staggered sequence of edge-sharing in the TiO_6 chain along the *c* axis of $Ti(OCH_2CH_2O)_2$ is very similar to that seen in the anatase structure. Therefore, a topotactic change

(20) Herrerous, B.; Barr, T. L.; Klinowski, J. *J. Phys. Chem.* **1994**, *98*, 738.
(21) Nishizawa, H.; Katsube, M. *J. Solid State Chem.* **1997**, *131*, 43.
(22) Doeuff, S.; Henry, H.; Sanchez, C. *Mater. Res. Bull.* **1990**, *25*, 1519.

from $Ti(OCH_2CH_2O)_2$ to TiO_2 (anatase) can be anticipated and will be reported elsewhere.

Conclusions

Despite the real and potential applications of metal alkoxides, successful synthesis and structural characterization of such materials remains a challenge for us. In this paper, single crystals of the titanium glycolate complex $Ti(OCH_2CH_2O)_2$ with a unique one-dimensional structure have been synthesized successfully by using hydrothermal methods. The alkalinity of the initial reaction mixture is a dominant factor for the product crystallization. The ethylene glycol serves not only as a solvent but also as a bidentate chelate occupying sites on the titanium coordination sphere so as to bridge adjacent titanium atoms and form the one-dimensional structure. This distinct bridging pattern somewhat passivates the surface of chains and leads to the high moisture stability of the crystal.

Upon calcination at higher temperatures, the product looses about 50% of its weight and is converted to titanium dioxide probably by a topotactic reaction.

Supporting Information Available: Tables of experimental conditions and crystal data, atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and hydrogen atom positions for $Ti(OCH_2CH_2O)_2$; tables of structure factors. This material is available free of charge via the Internet at http://puts.acs.org.

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