DOI: 10.1002/ejic.200700493

Environmentally Friendly Growth of Layered $K_4Nb_6O_{17}$ Crystals from a KCl Flux

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Keywords: Flux growth / Environmental chemistry / Layered compounds / Photocatalyst

Environmentally friendly, high-quality layered $K_4Nb_6O_{17}$ crystals were easily grown by two different flux methods involving supersaturation, that is, flux evaporation and cooling of the solution. To fabricate them, potassium chloride (KCl) was chosen as the flux. Transparent and colorless plate-like layered crystals of $K_4Nb_6O_{17}$ were prepared with well-developed {010} faces of the orthorhombic system. The crystal sizes obviously depended on the evaporation loss (evaporation method), the holding temperature, and the cooling rate (cooling method). Transmission electron microscopy (TEM) images showed that the grown plate-like crystals were of a very good crystallinity. The major constituents were homogeneously distributed throughout them. The crystals exhibited good photocatalytic activity under ultraviolet light irradiation. Potassium chloride was found to be a very suitable flux for the environmentally friendly growth of photocatalytic $K_4Nb_6O_{17}$ crystals.

Introduction

A variety of metal oxide compounds were studied for use as semiconductor photocatalysts, such as degradation of toxic substances, decomposition of pure water, and photoactive electrodes for dye-sensitized solar cells.[1–5] Photoinduced decomposition of pure water on TiO_2 electrodes was first reported in 1972.[4a] After this discovery, TiO_2 was widely studied, and has now became one of the most well-known semiconductor photocatalysts. Titanium(IV) oxide has several advantages, for example, it is harmlessness to the environment, it has a low cost, and it is highly stable. It, however, does not work efficiently as a photocatalyst under visible light irradiation, because it has a relatively wide bandgap of 3.0–3.2 eV.[4] Numerous attempts have, therefore, been made to improve its performance under visible light irradiation. In a few decades, several kinds of metal oxides, such as titanates, niobates, tantalates, and multioxides have also been found to exhibit photocatalytic performance.

The crystal of potassium hexaniobate ($K_4Nb_6O_{17}$), which is one kind of metal niobate, is orthorhombic with the space group $P2_1nb$.[6a] $K_4Nb_6O_{17}$ was reported to have lattice parameters of $a = 0.783$ nm, $b = 3.321$ nm, and $c = 0.646$ nm, and a density of 3.898 $g\,cm^{-3}$.[3,6a] The congruent melting point of this compound is 1163 °C.[7] From a crystal structure viewpoint, $K_4Nb_6O_{17}$ is unique in that it is layered (Figure 1),[6b] and it consists of negatively charged sheets of linked NbO_6 octahedral units with potassium ions between the sheets. A variety of characteristics of the layered $K_4Nb_6O_{17}$ crystals, such as their ability to undergo ion exchange and photocatalysis, as well as their intercalation properties, are attributed to their unique crystal structure (layered structure).

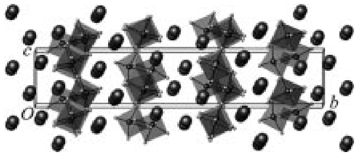

Figure 1. Schematic representation of the layered structure of $K_4Nb_6O_{17}$.

There have been many studies on $K_4Nb_6O_{17}$ crystallite syntheses and single crystal growth including flux growth, the Czochralski method, and solid-state reactions.[1,5a,8,9] Among these techniques, flux growth is an environmentally friendly process[10] and can produce $K_4Nb_6O_{17}$ crystals at temperatures below the melting point of the solute. In previous research, the following fluxes were used successfully: K_2CO_3, K_2MoO_4, and K_2WO_4.[5a,8] For the K_2CO_3 flux, however, detailed results such as the optimal growth conditions, crystal structure, size, and photocatalytic activity have not been described.[8] In our previous study,[5a] $K_4Nb_6O_{17}$

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crystals were grown from K_2MoO_4 and K_2WO_4 fluxes, and their photocatalytic and adsorption properties were examined in detail. Here we report the growth of high-quality $K_4Nb_6O_{17}$ plate-like crystals from a KCl flux at a growth temperature much less than the melting point of $K_4Nb_6O_{17}$. Furthermore, their photocatalytic properties were also evaluated. Potassium chloride has some advantages for the growth of $K_4Nb_6O_{17}$ crystals; its melting point (776 °C) is much lower than those of K_2CO_3 (891 °C), K_2MoO_4 (about 930 °C), and K_2WO_4 (921 °C) fluxes.[11–13] In addition, it has a common cation (K^+) with the solute. It is abundant in nature and is also harmless to human beings and the environment, much like NaCl. Furthermore, KCl is easily soluble in warm water. Until now, no report on the growth of $K_4Nb_6O_{17}$ crystals from a KCl flux has been published.

Results and Discussion

Photocatalytic, layered, transparent, and colorless plate-like crystals of $K_4Nb_6O_{17}$ were grown from the KCl flux (Table 1, all growth runs). In addition, byproduct crystals of $KNbO_3$ (bulk) and $K_2Nb_8O_{21}$ (whisker) were also grown in runs 1 and 10, and in run 4, respectively. The typical $K_4Nb_6O_{17}$ crystals (Table 1, run 1, solute concentration = 1 mol-%, holding temperature = 1100 °C) grown by the evaporation of the KCl flux isothermally are shown in Figure 2. Well-developed layered crystals of $K_4Nb_6O_{17}$ were clearly observed, and printed characters beneath the crystals were obviously readable. Moreover, numerous small plate-like crystals were relatively regularly layered on the well-developed surface, and the growth process was implied on the grown $K_4Nb_6O_{17}$ surface (Figure 2b). The SEM photographs of typical layered $K_4Nb_6O_{17}$ crystals are shown in Figure 3. The holding temperatures are, respectively, (a) 900 (Table 1, run 6), (b) 1000 (Table 1, run 5), and (c) 1100 °C (Table 1, run 3). The grown crystals gradually adopted rounded corners with decreasing holding temperatures as clearly shown in Figure 3. The evaporation loss of the KCl flux increased with the holding temperatures. The crystal sizes were obviously dependent on the flux evaporation ratio (and the holding temperature). In general, flux evaporation had a considerable influence on crystal growth. In the case where the holding temperature was 900 °C, the flux evaporation loss and the median diameter (D50) were, respectively, only approximately 34 wt.-% and 11.2 µm. However, they drastically increased with holding temperature, reaching about 86 wt.-% and 30.3 µm at 1000 °C, and 96 wt.-% and 27.6 µm at 1100 °C. The crystals grown at the holding temperature of 1000 °C might be slightly larger than those grown at 1100 °C, because the evaporation rate of the KCl flux at 1000 °C was smaller than that at 1100 °C. In general, crystals could grow large when the evaporation rate was suitable. When the holding temperature was 900 °C or below, the driving force for crystal growth could not distinguish between flux evaporation and solution cooling (rapid cooling) after a power supply cut of the furnace, as the evaporation loss was sufficiently low.

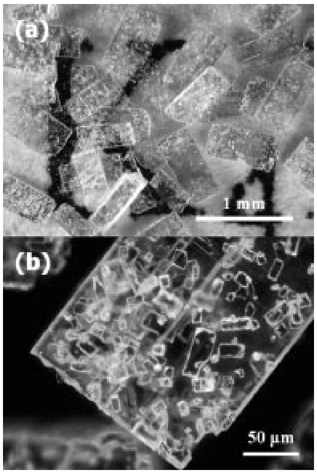

Figure 2. Optical micrographs showing plate-like $K_4Nb_6O_{17}$ crystals grown by the evaporation of a KCl flux: (a) low magnification and (b) high magnification.

Figure 4 shows the typical $K_4Nb_6O_{17}$ crystals grown by the cooling of the KCl flux (Figure 4a and b, Table 1, run 11; Figure 4c and d, Table 1, run 12). Like the $K_4Nb_6O_{17}$ crystals grown by the evaporation method (Figures 2 and 3), their basic form was a well-developed thin plate. There were a great number of the small plate-like crystals in the

Table 1. Typical growth conditions of the $K_4Nb_6O_{17}$ crystals.

Run No.	Solute concentration / mol-%	Solute K_2CO_3 / g	Solute Nb_2O_5 / g	Flux KCl / g	Holding temperature / °C	Holding time / h	Cooling rate / °C h^{-1}
1	1	0.826	2.383	22.054	1100	60	–
2	10	4.171	12.033	10.124	1100	60	–
3	20	5.382	15.526	5.806	1100	60	–
4	40	6.297	18.166	2.546	1100	60	–
5	20	5.382	15.526	5.806	1000	60	–
6	20	5.382	15.526	5.806	900	60	–
7	20	5.382	15.526	5.806	1000	5	60
8	20	5.382	15.526	5.806	900	5	60
9	20	5.382	15.526	5.806	800	5	60
10	20	5.382	15.526	5.806	700	5	60
11	20	5.382	15.526	5.806	800	5	300
12	20	5.382	15.526	5.806	800	5	>10000

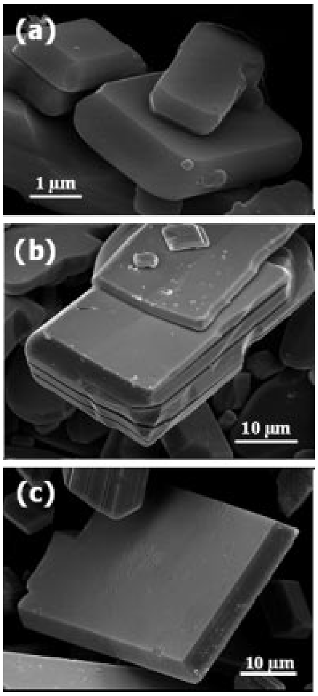

Figure 3. SEM images showing typical layered plate-like $K_4Nb_6O_{17}$ crystals grown by the evaporation of a KCl flux [holding temperature: (a) 900, (b) 1000, and (c) 1100 °C].

SEM image, although only a few of the relatively large crystals (>1 µm) were observed. However, relative to the evaporation method, the median diameters decreased drastically. Figure 5 shows the variation in the median diameter of the $K_4Nb_6O_{17}$ crystals grown by the cooling of the KCl flux with (a) the holding temperature and (b) the cooling rate. The cooling rate and the holding temperature were fixed at 60 °C h^{-1} and 800 °C in Figure 5a and b, respectively. Small crystals with D50 = 1.0 µm were grown at a holding temperature of 800 °C (Figure 5a). The D50 values gradually increased with increasing holding temperatures, and they reached about 5.0 µm (900 °C) and 24.5 µm (1000 °C). In contrast, the median diameter gradually decreased with an increase in the cooling rate, and it reached 0.5 µm at 300 °C h^{-1} and 0.4 µm at quenching (Figure 5b). In the previous studies, $K_4Nb_6O_{17}$ crystals were grown from a K_2CO_3 flux and by the Czochralski method at temperatures in excess of their melting points, or from K_2MoO_4 and K_2WO_4 fluxes at temperatures in excess of 1100 °C (in our laboratory). In this study, however, high-quality $K_4Nb_6O_{17}$ crystals were successfully grown from a KCl flux at temperatures from 800 to 1100 °C. To make environmentally functional materials, it is very important to reduce the environmental load. A low-temperature/rapid-cooling process is more environmentally friendly than other high-temperature flux ones[8] and our previous slow cooling one.[5a]

Figure 6 shows the XRD profiles of data for the well-developed layered crystals grown by the evaporation method (Figure 6a), pulverized crystallites grown by the evaporation method (Figure 6b) and by the cooling method (Figure 6c), and $K_4Nb_6O_{17}$ ICDD PDF[6] (Figure 6d). Both the grown crystals had approximately the same XRD pattern as ICDD PDF,[6] and they were identified as $K_4Nb_6O_{17}$. Byproduct crystals of $KNbO_3$ and $K_2Nb_8O_{21}$ were also identified by powder XRD patterns.[14,15] In our previous study,[5a] layered $K_4Nb_6O_{17}$ crystals were bound by two basal and eight sided faces. The indices of well-developed basal faces were {010}. In this study, the XRD patterns of oriented plate-like crystals showed that the diffraction intensity of the (040) plane was predominant, and the indices were the same as our previous study. Figure 7a and b show a bright field TEM image and the corresponding selected area diffraction (SAD) pattern of a typical crys-

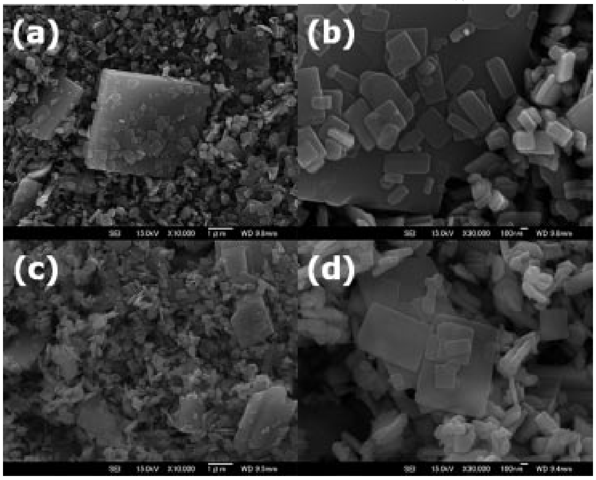

Figure 4. SEM images showing typical layered plate-like $K_4Nb_6O_{17}$ crystals grown by the rapid cooling of a KCl flux: (a) low magnification and (b) high magnification (Table 1, run 11, holding temperature 800 °C and cooling rate 300 °C h^{-1}), (c) low magnification and (d) high magnification (Table 1, run 12, 800 °C and quenching).

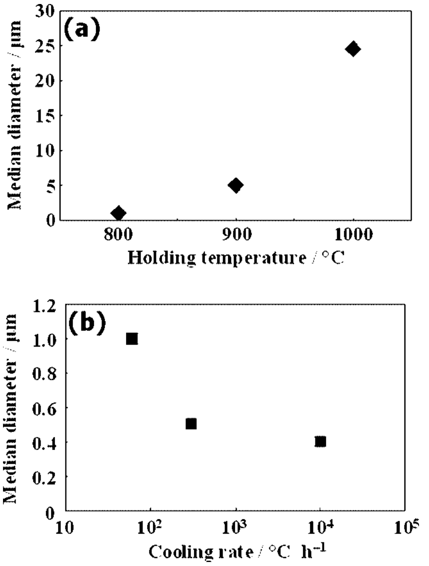

Figure 5. Variation in the median diameter of the $K_4Nb_6O_{17}$ crystals with (a) holding temperatures (solute content 20 mol-%, cooling rate 60 °C h^{-1}) and (b) cooling rates (solute content 20 mol-%, holding temperature 800 °C).

tal grown by the flux evaporation method (Table 1, run 2). In Figure 7a, the existence of some facets, which are related to the *a* and *c* planes, is evidently observed at the upper, lower, and right regions. The SAD pattern indicated that the crystal has orthorhombic symmetry with lattice parameters a = 0.769 nm and c = 0.639 nm, which are in good agreement with those found in the previous study.[6] Because the incident electron beam is parallel to the [010] direction, the lattice parameter *b* cannot be measured by only this incident beam. The crystal planes in the SAD pattern were confirmed to be in accordance with a $K_4Nb_6O_{17}$ layered structure. The lattice image obtained from a $K_4Nb_6O_{17}$ crystal is shown in Figure 7c, which was taken with the incident beam along the [010] direction. The crystal was of very good crystallinity because no defects were observed in this image. From these TEM observations, the development of the *a*–*c* plane was clearly observed. With the consideration of the lattice parameters (extremely long *b* axis), it seems reasonable to develop the plane, and moreover, this is in good agreement with previous research[5a] and the XRD results as mentioned above. Additionally, the EDS data showed that potassium and niobium atoms were homogeneously distributed in the crystals. Chlorine atoms from the flux were not detected in the crystals.

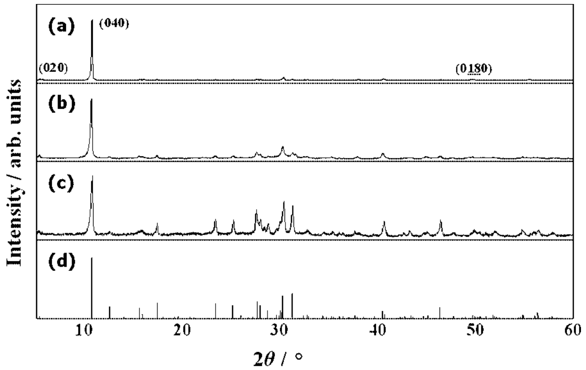

Figure 6. X-ray diffraction patterns (Cu-K_α) of $K_4Nb_6O_{17}$ crystals: (a) plate-like crystals of which well-developed faces were laid in parallel with the holder plate (Table 1, run 4), (b) pulverized crystallites (evaporation method; Table 1, run 3), (c) pulverized crystallites (cooling method; Table 1, run 9), and (d) $K_4Nb_6O_{17}$ ICDD PDF.[6a]

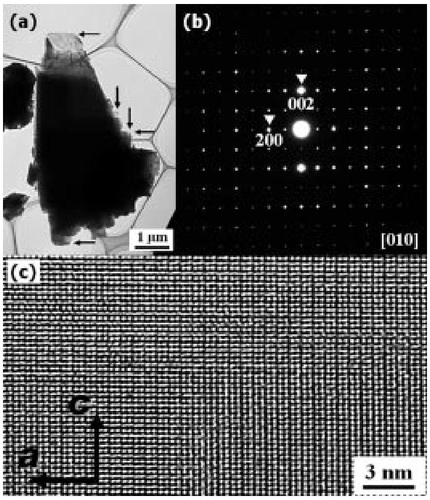

Figure 7. (a) TEM micrograph, (b) diffraction pattern, and (c) lattice image of a typical plate-like $K_4Nb_6O_{17}$ crystals.

The UV/Vis diffuse reflectance spectrum of the $K_4Nb_6O_{17}$ crystals was investigated. The spectrum (Figure 8) shows the onset wavelength of absorption at around 365 nm and a maximum at around 250 nm. Typical absorption spectra of TiO_2 (anatase) powders and $Na_2Ti_6O_{13}$ whiskers shift, respectively, to longer wavelength by about 35 and 15 nm at the onset. This result is in fair accord with that of our previous studies.[5a,5b] Furthermore, the $K_4Nb_6O_{17}$ layered crystals acted efficiently as a photocatalyst under UV light irradiation, and the characteristic colors of organic dyes (e.g., methylene blue and methyl orange) faded by the photocatalytic effect. For example, the pulverized $K_4Nb_6O_{17}$ crystals (0.5 g) and methylene blue (0.25 mg) were placed in distilled water (100 cm^3). The suspension was irradiated with UV light for 0–9 h. In this case, the color of the suspension decolorized gradually with an increase in irradiation time and finally changed from blue to colorless. The color of the suspension irradiated with UV light for 9 h was unchanged by the addition of any acid or base. When no $K_4Nb_6O_{17}$ crystal was added, the color of the methylene blue solution with UV light for 9 h remained unchanged.

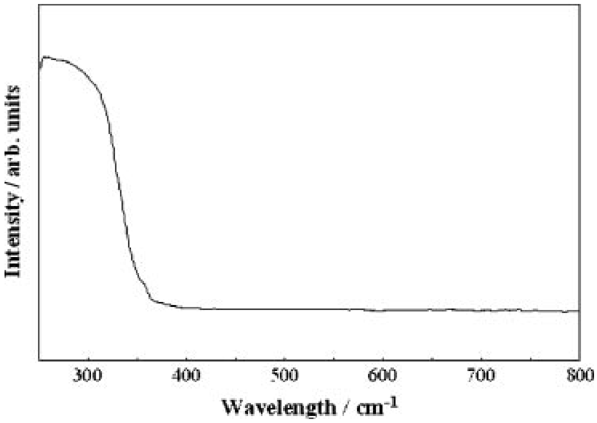

Figure 8. UV/Vis diffuse reflection spectrum of $K_4Nb_6O_{17}$ crystals.

Conclusions

Highly crystalline photocatalytic crystals of $K_4Nb_6O_{17}$ were successfully grown by the evaporation or the rapid cooling of KCl used as the flux. Furthermore, this low holding temperature (ca. 800 °C)/rapid cooling (≥300 °C h^{-1}) technique is more environmentally friendly than other high-temperature flux techniques[8] and our previous slow cooling method.[5a] The layered $K_4Nb_6O_{17}$ crystals were transparent and colorless, and they were plate-like in form with well-developed {010} faces (XRD analysis and TEM observation). The crystal sizes were dependent on the holding temperature and the cooling rate. In the case of the flux evaporation, the crystal sizes decreased gradually with a decrease in evaporation rate, and they reached 11.2 µm at 34 wt.-%. In contrast, for flux cooling, the crystal size drastically decreased with a decrease in holding temperature and gradually decreased with an increase in cooling rate, and the size was reduced to 0.4 µm (holding temperature of 800 °C and quenching). The obtained crystals had no defects (TEM observation) and major components were homogeneously distributed in the crystals (EDS analysis). Furthermore, plate-like layered $K_4Nb_6O_{17}$ crystals exhibited photocatalytic properties for organic dye decolorization. In our growth technique of functional oxide crystals, environmental damages (e.g., by exhausting greenhouse gases) and product costs are thought to be reduced greatly. In the future, it will become more and more important to develop various functional materials (including crystals) with the use of environmentally friendly processes.

Experimental Section

Potassium hexaniobate layered crystals were grown by a cooling method and an evaporation method of the KCl flux. Reagent grade K_2CO_3 (Wako Pure Chemical Industries, Ltd.), Nb_2O_5 (99.9%, Wako Pure Chemical Industries, Ltd.), and KCl (Wako Pure Chemical Industries, Ltd.) were used for the growth of the $K_4Nb_6O_{17}$ crystals. A stoichiometric mixture of K_2CO_3 and Nb_2O_5 powders and KCl were, respectively, used as a solute and flux. The typical growth conditions are given in Table 1.

Flux Evaporation Method: The solute concentration was varied from 1 to 40 mol-% of the KCl flux. These masses of the reagents were kept at approximately 25 g for all growth runs (Table 1, runs 1–6). Each of the mixtures was put into platinum crucibles of 30-cm^3 capacity. After the lids were loosely closed, the crucibles were placed in an electric furnace. The crucibles were heated to 900, 1000, or 1100 °C at a rate of 45 °C h^{-1} and then held at each temperature for 60 h. Subsequently, the electric power was turned off, and the crucible was cooled quickly to room temperature in the furnace.

Cooling Method: The crucibles containing each mixture (Table 1, runs 7–12) were heated to 700, 800, 900, or 1000 °C at a rate of 45 °C h^{-1} and held at each temperature for 5 h. The crucibles were then cooled to 500 °C at a rate of 60, 300, or $>$10000 (quenching) °C h^{-1}. The cooling rates of 60 and 300 °C h^{-1} were controlled by the cooling program, and the crucibles were cooled to room temperature in the furnace. The cooling rate of $>$10000 °C h^{-1} was not able to be attained by the cooling program in the furnace. For $>$10000 °C h^{-1}, the crucibles were held at 800 °C for 5 h, and then removed from the furnace and cooled rapidly to room temperature (quenching in air). In both cases (flux evaporation and cooling), the crystal products were separated from the remaining flux in warm water.

The obtained crystals were observed by an optical microscope and field emission scanning electron microscope (FE-SEM, JEOL, JSM-7000F). Phases and elongated directions of the crystals were studied by X-ray diffraction (XRD, SHIMADZU, XRD-6000). An energy-dispersive X-ray spectrometer (EDS, HORIBA, EMAX-5770Q) was used to study any variation in the concentration of the major constituents in the grown crystals. The presence of impurities from the KCl flux and platinum crucible was also observed. The high-resolution transmission electron microscopy (HRTEM) and electron diffraction observations were carried out with JEM-2010 (JEOL) and JEM-2000EXII (JEOL) instruments operated at 200 kV to analyze the crystallinity and elongated direction of the grown crystals. The average sizes were measured with a laser diffraction particle size analyzer (SHIMADZU, SALD-300V). The ultraviolet/visible (UV/Vis) light diffuse reflectance spectrum of the grown crystals was obtained with a spectrophotometer (SHIMADZU, UV3150). Photocatalytic properties of the grown crystals were examined by the photodecolorization of aqueous organic dyes under an atmosphere.[5a,5b] The UV light source employed in this study was a commercial black light (15 W × 2). The center wavelength of the UV light was 352 nm.

Acknowledgments

This research was partially supported by the TEPCO Research Foundation and The Salt Science Research Foundation, No.0609 and No.0706. A part of this work was performed under the inter-university cooperative research program of Advanced Research Center Metallic Glasses, Institute for Materials Research, Tohoku University.

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[1] a) K. Domen, A. Kudo, A. Shinozaki, A. Tanaka, K. Maruya, T. Onishi, *J. Chem. Soc. Chem. Commun.* **1986**, 356–357; b) T. Nakato, K. Kuroda, C. Kato, *J. Chem. Soc. Chem. Commun.* **1989**, 1144–1145.

[2] a) Y. Inoue, T. Kubokawa, K. Sato, *J. Chem. Soc. Chem. Commun.* **1990**, 1298–1299; b) J. Ramirez-Salgado, E. Djurada, P. Fabry, *J. Eur. Ceram. Soc.* **2004**, *24*, 2477–2483.

[3] a) H. Kato, A. Kudo, *Chem. Phys. Lett.* **1998**, *295*, 487–492; b) M. Machida, J. Yabunaka, T. Kijima, *Chem. Commun.* **1999**, 1939–1940; c) K. Shimizu, Y. Tsuji, T. Hatamachi, K. Toda, T. Kodama, M. Sato, Y. Kitayama, *Phys. Chem. Chem. Phys.* **2004**, *6*, 1064–1069.

[4] a) A. Fujishima, K. Honda, *Nature* **1972**, *238*, 37–38; b) M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.* **1995**, *95*, 69–96.

[5] a) K. Teshima, K. Horita, T. Suzuki, N. Ishizawa, S. Oishi, *Chem. Mater.* **2006**, *18*, 3693–3697; b) K. Teshima, K. Yubuta, S. Sugiura, T. Suzuki, T. Shishido, S. Oishi, *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1725–1728; c) K. Teshima, D. Tomomatsu, T. Suzuki, N. Ishizawa, S. Oishi, *Cryst. Growth Des.* **2006**, *6*, 18–19.

[6] a) ICDD-PDF 76–977; b) M. Gasperin, M. T. Le Bihan, *J. Solid State Chem.* **1982**, *43*, 346–353.

[7] E. M. Levin, C. R. Robbins, H. F. McMurdie in *Phase Diagrams for Ceramists*, The American Ceramic Society, Westerville, OH, **1964**, fig. 171, p. 88.

[8] M. Kestigian, F. D. Leipziger, J. R. Carter, F. G. Garabedian, *J. Am. Ceram. Soc.* **1966**, *49*, 517.

[9] K. Nassau, J. W. Shiever, J. L. Bernstein, *J. Electrochem. Soc.* **1969**, *116*, 348–353.

[10] a) S. Oishi, K. Teshima, H. Kondo, *J. Am. Chem. Soc.* **2004**, *126*, 4768–4769; b) K. Teshima, A. Takano, T. Suzuki, S. Oishi, *Chem. Lett.* **2005**, *34*, 1620–1621; c) K. Teshima, K. Yubuta, S. Sugiura, Y. Fujita, T. Suzuki, M. Endo, T. Shishido, S. Oishi, *Cryst. Growth Des.* **2006**, *6*, 1598–1601; d) K. Teshima, Y. Kikuchi, T. Suzuki, S. Oishi, *Cryst. Growth Des.* **2006**, *6*, 1766–

1768; e) K. Teshima, K. Yubuta, S. Ooi, T. Suzuki, T. Shishido, S. Oishi, *Cryst. Growth Des.* **2006**, *6*, 2538–2542.

[11] E. M. Levin, H. F. McMurdie in *Phase Diagrams for Ceramists 1975 Supplement*, The American Ceramic Society, Westerville, OH, **1975**, fig. 4889, p. 392.

[12] E. M. Levin, C. R. Robbins, H. F. McMurdie in *Phase Diagrams for Ceramists*, The American Ceramic Society, Westerville, OH, **1964**, fig. 176, p. 89.

[13] E. M. Levin, C. R. Robbins, H. F. McMurdie in *Phase Diagrams for Ceramists*, The American Ceramic Society, Westerville, OH, **1964**, fig. 177, p. 90.

[14] ICDD-PDF 32–822.

[15] ICDD-PDF 31–1060.

Received: May 8, 2007