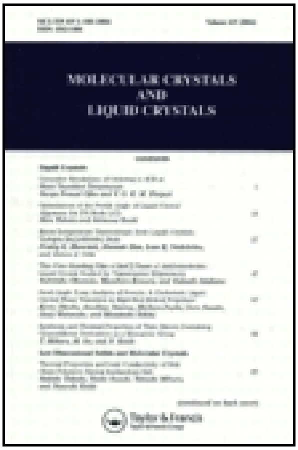

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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To cite this article: Takayoshi Sasaki & Mamoru Watanabe (1998): X-Ray Diffraction Study on Crystalline and Osmotic Swelling of a Layered Titanate, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 311:1, 417-422

To link to this article: http://dx.doi.org/10.1080/10587259808042419

Mol. Cryst. Liq. Cryst., 1998, Vol. 311, pp. 417–422
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X-Ray Diffraction Study on Crystalline and Osmotic Swelling of a Layered Titanate

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The swelling of a layered protonic titanate $H_{0.7}Ti_{1.825}\square_{0.175}O_4\cdot H_2O$ ($\square$: vacancy) upon contact with the system of tetrabutylammonium (TBA) ion and H_2O has been studied by X-ray diffraction. The TBA-intercalated titanate revealed three distinct gallery heights of 1.47, 1.75 and 2.1 nm, depending on water vapor pressure and drying temperature. These are attributable to crystalline swelling, i. e., zero-, mono- and bi-layer hydrates.

A much higher degree of hydration was discerned by a series of sharp diffraction lines for a colloidal aggregate centrifuged from an aqueous suspension of the titanate and TBA ion. The basal spacing expanded steadily from 4 to >20 nm with decrease of the TBA concentration. Along this osmotic swelling process, amorphouslike halo was evolved, which suggests exfoliation into single sheets.

Keywords: layered titanate, hydration, crystalline swelling, osmotic swelling, exfoliation

INTRODUCTION

Hydration of layered compounds is of great importance because it provides useful information on host-guest and guest-guest interactions. Clay minerals have been studied extensively from such a viewpoint, through which three types of hydration, crystalline swelling, osmotic swelling and exfoliation, have been demonstrated[1-4].

There are a class of layered titanates and we have examined preparations of their protonic forms and intercalation reactions[5-8]. Hydration in the presence of TBA ion is of interest because action of its aqueous solution facilitates delamination of the protonic titanate with the lepidocrocite-type structure into single sheets[9]. The present study is undertaken to obtain systematic view on hydration behavior from crystalline swelling to osmotic swelling and exfoliation.

EXPERIMENTAL

The protonic oxide with the lepidocrocite-like layered structure, $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$, was synthesized by acid-exchange of a Cs-titanate, $Cs_{0.7}Ti_{1.825}\square_{0.175}O_4$, which was obtained through solid-state calcination of Cs_2CO_3 and TiO_2 at 1073 K[7,10].

The hydration process was followed by X-ray diffraction (XRD) using a Rigaku 2000 diffractometer equipped with a specially designed humidity-controllable sample chamber.

RESULTS AND DISCUSSION

Formation of the TBA-Intercalated Complex and Its Hydration

The TBA-intercalated titanate could not be obtained by a conventional procedure involving solid-solution interaction followed by filtration and drying, because $H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot H_2O$ spontaneously forms a stable colloidal suspension upon contact with a TBA aqueous solution[9]. As an alternative route, freeze-drying of the suspension produced the intercalated complex of composition $((C_4H_9)_4N)_{0.3}H_{0.7}Ti_{1.825}\square_{0.175}O_4 \cdot 0.7H_2O$ with an intersheet repeat distance of 1.75 nm[11]. Although we carried out syntheses from the suspensions containing various amount of TBA ions, the products were similar in terms of stoichiometry as well as gallery height, which suggests that excess TBA ions were removed by freeze-drying.

Figure 1 shows XRD patterns in the heating process of the TBA-intercalated phase. Neither significant change in basal spacing (1.75 nm) nor in weight was observed up to 373 K. The shrinkage by 0.28 nm took place in the temperature range of 373 - 423 K. A concurrent weight loss of 5.5 % is compatible with removal of 0.7 mol of H_2O per chemical formula of the complex above. The dehydrated phase was stable up to 473 K where it began to be degraded.

The 1.75 nm phase underwent stepwise swelling when brought into contact with an ambient atmosphere having a higher water vapor pressure (see Fig. 2). Each curve was obtained after conditioning the sample at a certain relative humidity for 1 hour. At a relative humidity below 60 %, the intersheet spacing was substantially constant in the range of 1.75 - 1.80 nm. A discontinuous expansion took place around 70 %, which suggests the presence of a hydrate structure characterized by the gallery height of 2.1 nm. Gravimetry indicates insertion of ~1 mol of H_2O per formula unit.

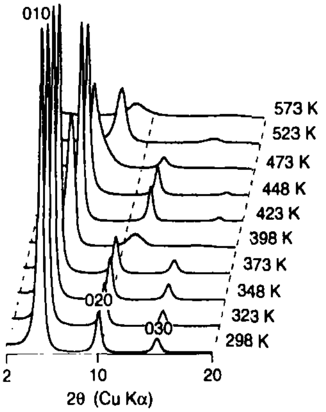

FIGURE 1 XRD data for the TBA intercalated titanate as a function of heating temperature.

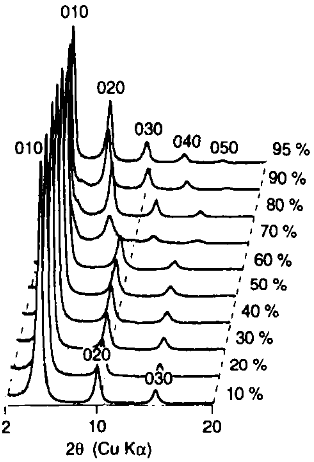

FIGURE 2 XRD data as a function of relative humidity at 303 K.

Subsequent humidification gave rise to a continuous swelling to 2.7 nm at 95 %, which may be interpreted as a beginning stage of osmotic swelling.

Structure of the TBA-Intercalated Titanate Hydrates

The geometry of TBA ion is illustrated in Figure 3. A length of the chain is estimated to be 0.73 nm from the literature[12] (= 0.61 nm for n-butylamine + 0.12 nm for van der Waals radius of H atom). Two models for orientation of the interlayer TBA ion may be considered; alignment of pseudo C_2 or C_3 axis of the guest perpendicular to the host sheet. The intersheet expansion for each orientation is expected to be 0.84 nm and 0.97 nm, respectively. The observed data of 0.81 nm (= 1.75 - 0.94) suggests that TBA ions are incorporated in the former orientation together with monolayer H_2O as shown in Figure 4[13]. Note that the parent titanate accommodates H_2O molecules and H_3O^+ ions in monolayer arrangement, giving the interlayer distance of 0.94 nm[7]. Based on the accommodation model (Fig. 4) where TBA ions are 'closely' packed in the gallery, the packing density is calculated to be 0.35 nm^2 (= 1.19 x 1.19 / 4) per guest cation. Since the unit interlayer space encircles a host-sheet surface area of 0.114 nm^2 (= 0.38 x

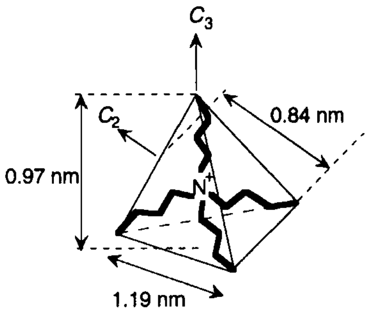

FIGURE 3 Molecular Structure of TBA ion.

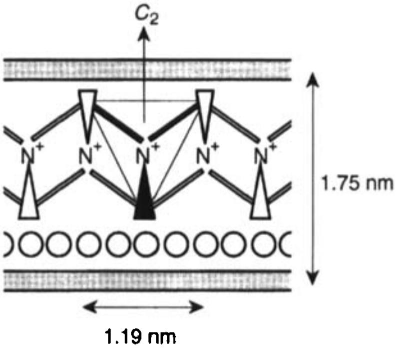

FIGURE 4 Plausible model for the TBA intercalated phase. Lanky triangles and rectangles denote C_4H_9 chains while circles express H_2O molecules. One of TBA ions is highlighted for clarity.

0.30)[7], the theoretical stoichiometry should be 0.32 (= 0.114 / 0.35), which shows excellent agreement with the chemical composition determined experimentally.

The discrete gallery heights of 1.47, 1.75 and 2.1 nm can be understood by accommodation of integral numbers of H_2O layers co-intercalated with TBA ions, which are reasonable both from structural and compositional aspects. Similar hydration series have been reported for titanates[5-7], transition metal dichalcogenides[14] and clay minerals[1,2] having alkali metal ions as interlayer guests.

Osmotic Swelling and Exfoliation

Interaction between the titanate and TBA aqueous solutions gave rise to an extremely high degree of hydration, or formation of a colloidal suspension. We prepared the suspensions by shaking 1 g of the titanate with 250 cm^3 of TBA solution of various concentrations. A glue-like aggregate was centrifuged from them and allowed to XRD measurements at the high relative humidity of 95 % to keep it from drying. Several orders of sharp reflections were observed in a small-angle scattering region, which is assignable to an osmotically swollen phase. The basal spacing was around 4 nm for a colloid at a high dose of TBA ions (see Fig. 5a). The intersheet expansion proceeded further to exceed 20 nm on decreasing the electrolyte concentration. This suggests that several tens of H_2O layers are accommodated in the intersheet domain.

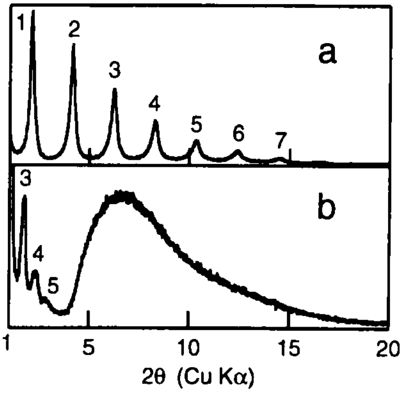

FIGURE 5 XRD data for a colloidal aggregate centrifuged from suspensions. The molar ratio of TBA/H in titanate is 25 in (a) and 2 in (b). Numerals designate the order of the basal diffraction series.

Hydration with swelling of this magnitude has not been reported for other layered hosts except for smectite clay minerals. Along with this process, an amorphouslike halo in 2θ range of 5 - 15° became pronounced, which was accompanied by apparent decline of the osmotically swollen component as exemplified by Fig. 5b. This broad diffraction feature may be attributable to scattering from a pile of exfoliated elementary sheets which are closely assembled like liquids as a result of centrifugation. These phenomena lead to the conclusion that osmotic swelling promotes exfoliation into single sheets especially at a low ionic strength. Detailed analysis of osmotic swelling and exfoliation process is now under way.

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