

Selected Paper

Calorimetric Finding of Phase and Glass Transitions Concerning the Ordering of the Water Located between the Silicate Layers of the Clay Na-RUB-18

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The behavior of the water accommodated between the silicate layers of a clay $Na_8[Si_{32}O_{64}(OH)_8]\cdot 32H_2O$ was investigated by using adiabatic calorimetry. A phase transition was observed showing a heat-capacity peak at 194 K and its entropy was roughly estimated to be 5.2 J K^{-1} (H_2O-mol)$^{-1}$. The transition was interpreted to be essentially due to an order–disorder process involving two orientations of the water molecule which can form hydrogen bonds with siloxane-oxygen atoms. It is thought that the water molecules move with a large amplitude of vibration as well as disorder between the two permissible orientations at room temperature and become gradually ordered to take a more stable orientation of the two below 194 K. A glass transition was found at a temperature $T_g = 106$ K, due to freezing of the water molecule in the orientations, which causes a little disorder to remain. The potential barrier ($\Delta\varepsilon_a$) of the reorientation was assessed from the T_g to be about 34 kJ mol^{-1}, which corresponds to the energy to break two hydrogen-bonds. There remains a possibility that the silanol-hydrogen atom takes a tunneling state involving two accessible sites between two silanol-oxygen atoms; however, it was not confirmed in this work.

Many compounds have a layered structure and include water molecules in between the layers. Clays are typical among the compounds. Montmorillonite,[1] as an example, can accommodate a rather arbitrary number of water molecules, and its property is considered to produce the functional character of the clays. $Na_8[Si_{32}O_{64}(OH)_8]\cdot 32H_2O$ (hereafter named Na-RUB-18), which is a type of clay, is a counterpart to such clays. Even though an abundant amount of water is added to it, no more water molecules than specified can be inserted between the layers. Excess water and Na-RUB-18 containing the specified number of water molecules separate as different phases. Water molecules between the silicate layers are tightly bound in their positions and orientations.[2] The reason why some can accommodate a lot of water molecules, whereas the others cannot, is intriguing, and it is attractive to clarify the configuration and mobility of the water molecules in the whole range of clays at ambient and other conditions.

Some studies have devoted to the clarification of the static and dynamic behaviors of the water molecules in the compounds with a layered structure. Kittaka et al.[3,4] have examined the dynamic properties of the water molecules in $V_2O_5\cdot nH_2O$ by using a quasi-elastic neutron scattering method and impedance-analysis and FT-IR methods. The study shows that the molecules have large translational and rotational mobility, similar to that of bulk water, in the range 298–253 K. Benesi et al.[5,6] have investigated the similar behavior in the clay kanemite by using a ^{2}H NMR T_1 relaxation method, which indicates that the nano-sheet water shows ice-like dynamics, forming a tetrahedral arrangement of water molecules. That is, the water molecules are mostly bound and immobile. However, only a little on the ordering/disordering of the water molecules as a function of temperature has been elucidated in those layered compounds. In the present study, the static and dynamic properties of the water molecules in the Na-RUB-18 were examined below room temperature by using adiabatic calorimetry. The Na-RUB-18 is known to have many silanol groups (hydroxy groups bonding to silicon atom) on the surface of silicate layers, and the atoms on the surface including the silanol groups are arranged with long-range order in a crystalline way, like in $V_2O_5\cdot nH_2O$, but differently from those in natural clay minerals.[2,7] Brenn et al.[8] have applied a pulse-field-gradient NMR experiment and have reported that the water molecules exhibit rotational mobility similar to those in bulk water and translational one appreciably as well. Wolf et al.,[9] utilizing two-dimensional NMR exchange measurement, have found that ^{1}H/^{29}Si CP MAS spectra change around 200 K implying occurrence of a phase transition. In the present work, the water molecules, probably without strong hydrogen bonds with silicate layers at room temperature, were found to show phase and glass transitions at low temperatures, and quite a difference was expected to exist between their properties at low and high temperatures.

Experimental

Sample Preparation. Na-RUB-18 was synthesized according to the procedure described in the literature.[10] Silica gel (70–130 mesh) purchased from Aldrich Co., Ltd. and reagent grade sodium hydroxide from Wako Pure Chemical Co., Ltd. were used without further purification. H_2O (105 g, 5.8 mol), SiO_2 (silica gel) (50.0 g, 0.780 mol), and NaOH (16.9 g, 0.422 mol) were put into a polytetrafluoroethylene vessel, and the vessel was sealed tight. The mixture was then allowed to react under hydrothermal condi-

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tions at 105 °C for 9 days. A muddy precipitate was obtained and washed with pure water to remove the remaining NaOH until the wash water became neutral. Two samples were employed in the present work: One was located in the coexistence with bulk water as it was synthesized and denoted by Na-RUB-18(wet), and the other was prepared by drying the wet sample in vacuum at 24 °C for 3 days and denoted by Na-RUB-18(anhydride). The sample was shown to have no water molecules while the silanol groups as left. Then, the sample was dried at 80 °C in vacuum for 3 days, and no change was observed in its weight.

X-ray Diffractometry. X-ray diffractometry was carried out at room temperature for both the samples with a powder X-ray diffractometer (Rint 2000, Rigaku Co., Ltd.) by using a Cu Kα line with additional voltage and electric current of 40 kV and 100 mA, respectively. Intensity data were collected between $2\theta =$ 2 and 35° with 0.04° steps at a scanning rate of 2° min^{-1}. The sample cell was made of quartz glass.

Adiabatic Calorimetry. Heat capacities were measured in the temperature range of 50–300 K with an adiabatic calorimeter by using an intermittent heating method.[11,12] The initial equilibrium temperature ($T_{e,i}$) of the cell was determined in the former thermometry period of 8 min, a specified quantity of electrical energy (ΔE) was supplied into the cell to increase the temperature by 1.7–2.5 K, and the final equilibrium temperature ($T_{e,f}$) of the cell was again determined in the latter thermometry period of 8 min. The energy-supply periods were ca. 10, 25, and 40 min at 50, 150, and 300 K, respectively. The gross heat capacity of the cell was evaluated using $\Delta E/(T_{e,f} - T_{e,i})$ at $T_{av} = (T_{e,f} + T_{e,i})/2$. The latter thermometry process served as the former one in the next set of heat capacity measurement. When spontaneous heat release or absorption effects appear due to glass or phase transitions, one observes the corresponding spontaneous temperature rise or fall, respectively, in the thermometry periods.[12,13] The release/absorption rates were estimated in the present work from the average temperature-drifts in the latter 4 min of the thermometry period, since the thermal equilibration of the calorimeter cell took about 2 min after each energy supply.

The Na-RUB-18(wet) sample was loaded into a calorimeter cell of 40.748 g. The mass of the sample was determined to be 14.410 g. After the heat capacity measurements of the wet sample were finished, the Na-RUB-18(anhydride) sample was obtained by detaching the lid of the calorimeter cell and drying the wet sample as described above. The mass of the anhydride sample obtained was determined to be 3.610 g. The mass of the total water in the wet sample was therefore calculated to be 10.800 g (14.410–3.610). The heat capacity measurements were then carried out for the anhydride sample. The excess bulk water present in the wet sample was estimated from its enthalpy of fusion to be (9.875 ± 0.010) g, and therefore, the water contained between the silicate layers was calculated to be (10.800–9.875 ± 0.010) = (0.925 ± 0.010) g resulting in the chemical formula $Na_8[Si_{32}O_{64}(OH)_8]\cdot(31.9 \pm 0.4)H_2O$ for Na-RUB-18 (wet). Considering the uncertainty in the estimation of the quantity of extra bulk water, the following analyses of heat capacities were executed assuming that the formula is given by $Na_8[Si_{32}O_{64}(OH)_8]\cdot 32H_2O$, namely, 0.928 g of inter-layer water and thus 9.872 g of excess bulk water were involved in the wet sample.

The inaccuracy and imprecision of the heat capacity measurements were estimated previously by using benzoic acid as a standard to be less than ±0.3 and ±0.06%, respectively.[12] Since the heat capacities of the inter-layer water in the wet sample is about 20% of those of the benzoic acid in the calibration case, the accuracy and the precision of the heat capacities derived of the water are estimated roughly to be ±1.5 and ±0.3%, respectively.

Results and Discussion

Layer Structure of Na-RUB-18. Figures 1a and 1b show the powder X-ray diffraction patterns, taken at room temperature, of Na-RUB-18(wet) and Na-RUB-18(anhydride), respectively. The intensities of the peaks in the anhydride were weaker than those of the wet sample, indicating that the removal of nano-sheet water destroys the strict long-range order in the arrangement of the silicate layers. The lowest-in-angle sharp peak observed at $2\theta = 7.7°$ corresponds to 11.1 Å and was assigned as the inter-layer distance of Na-RUB-18. The distance is almost same in the wet and anhydride samples. This means that the layered structure of Na-RUB-18 remains after the removal of hydration water. Figure 2 shows schematically the room-temperature crystal structure of hydrated

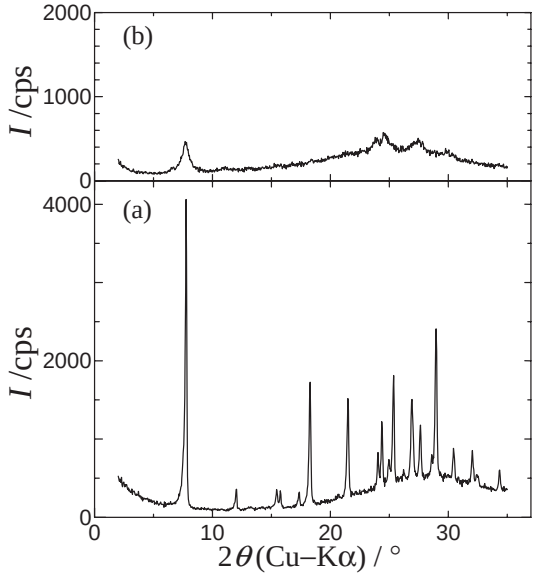

Fig. 1. Powder X-ray diffraction patterns of the Na-RUB-18(wet) (a) and Na-RUB-18(anhydride) (b).

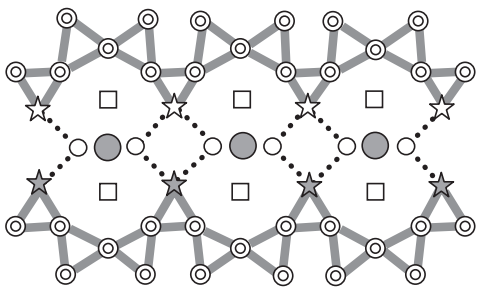

Fig. 2. Schematic drawing of the layered crystal structure, determined by Vortmann et al.[2] through an ab initio calculation based on powder X-ray diffraction data, of the Na-RUB-18: double circle, siloxane-oxygen atom; open and gray star, silanol-oxygen atom; gray circle, sodium atom; open circle and square, water molecules coordinated to sodium ions; dotted line, hydrogen bond; gray bar, oxygen–oxygen line for indicating silicate tetrahedron. Silicate and water layers are stacked in the *c* direction.

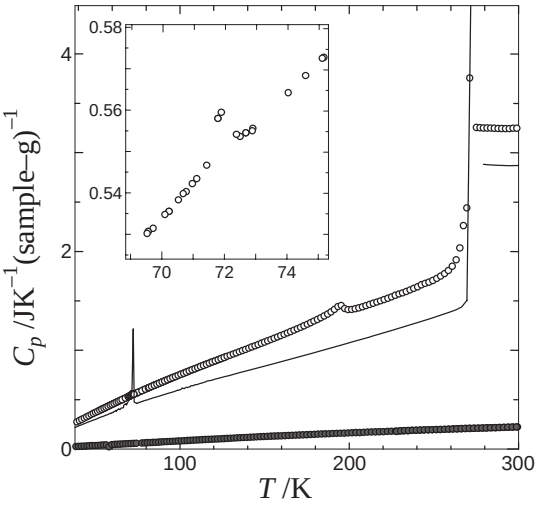

Fig. 3. Measured heat capacities per gram of Na-RUB-18(wet) sample: open circle, wet sample; filled circle, anhydride sample contained in a gram of the wet sample; solid line, bulk water/ice contained in a gram of the wet sample. Inset shows the heat capacities of the wet sample on an enlarged scale from 68 to 76 K.

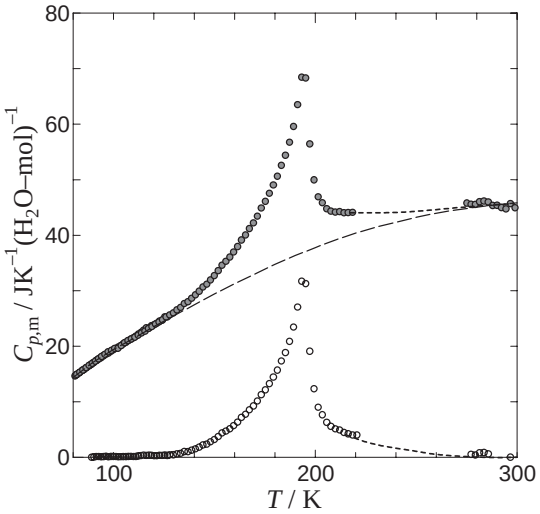

Fig. 4. Molar heat capacities of the water confined between the silicate layers in Na-RUB-18(wet): gray circle, experimentally derived; open circle, the excess due to the phase transition. The experimental values were derived by subtracting the heat capacities of the bulk water/ice[14] and the anhydride sample from those of the wet sample. The baseline was so drawn as to link smoothly the heat capacities around 100 and 290 K. The data in the range of 220–274 K were omitted from the plot, because the effect of the fusion of bulk ice including the eutectic one remained in the derived data so that they could not represent the true values of the compound Na-RUB-18.

Na-RUB-18, determined by Vortmann et al.,[2] as an ab initio structure solution from X-ray powder data. Double circle and star mark represent siloxane-oxygen and silanol-oxygen atoms forming silicate layers. Each sodium ion, indicated with a gray circle, is coordinated octahedrally by six water molecules represented by open circles and squares; the former water molecules form hydrogen bonds, as indicated with dotted lines, with silanol-oxygen atoms with O···O distance of 0.281 nm, and the latter are located far from silanol oxygen (O···O distance; 0.385 nm) not to form a hydrogen bond with it. Therefore, it is expected that the former water molecules bridging the silanol groups of neighboring silicate-layers is relevant for determining the separation between the neighboring layers in the hydrated Na-RUB-18. In the Na-RUB-18(anhydride), on the other hand, the water molecules were removed. There is a possibility that the silanol oxygen atoms coordinate sodium ions to combine the silicate layers and the inter-layer distance happens to be the same as the value in the hydrated Na-RUB-18.

Heat Capacities of the Water Located in between the Na-RUB-18 Silicate Layers. Open and closed circles in Fig. 3 represent the heat capacities of the wet and anhydride samples of Na-RUB-18, respectively, per gram of the former one. Solid line stands for the temperature dependence of the heat capacity of water/ice doped with KOH only of 10^{-3} mol dm^{-3};[14] the amount of the water/ice corresponds to that involved in 1 g of the wet sample. The inset shows the heat capacities of the wet sample on an enlarged scale in the range 69–75 K. The anhydride sample displayed no anomaly over the whole temperature range. On the other hand, three anomalies appeared at 273, 194, and 72 K in the wet sample. The first one is due to the fusion of bulk ice. The third is considered as due also to a phase transition of the extra bulk ice, as described below. The second is thought to be a phase transition due to Na-RUB-18. The reason is that the extra bulk water is in the crystalline state of ice at 194 K and no anomaly occurs in the ice. Considering that each silicate layer has a firm framework structure and that the configurational change of the silicate layers with temperature, if any, as their mutual relation makes no appreciable contribution to the calorimetry, the transition is understood furthermore as caused by a configurational change of water molecules including silanol groups. Therefore, recognizing the heat capacity observed of the wet sample as given by the sum of the three contributions from Na-RUB-18(anhydride), the water located between the silicate layers, and the extra bulk water/ice, the contribution of the inter-layer water was derived by subtracting those of Na-RUB-18(anhydride) and extra bulk water/ice[14] from the value obtained of Na-RUB-18(wet). Gray circles in Fig. 4 represent the derived values. The heat capacities around 220 and 290 K, below and above respectively the fusion temperature of bulk ice, can be linked reasonably smoothly, indicating that the estimation of the quantity of extra bulk water included was appropriate and reasonable. The anomaly with a peak at 194 K has a wide skirt both on the low- and high-temperature sides.

Figure 5 shows temperature dependence, below 255 K, of the spontaneous enthalpy release or absorption rates per mole of water between silicate layers in the wet sample: the rates were estimated as the average in the latter 4 min of the thermometry period of 8 min. No anomalous effect was observed around 194 K, indicating that the phase transition mentioned above is a second-order transition and exhibits no jump at 194 K in the thermodynamic and structural state. Anomalous effects were observed around 72, 100, and 240 K, respectively. The enthalpy absorption effect around 72 K corresponds to the

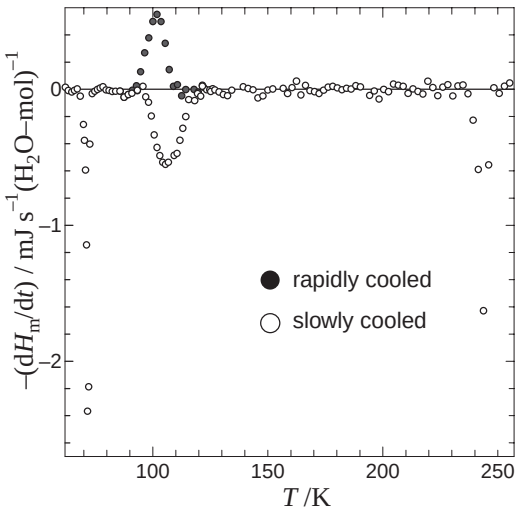

Fig. 5. Temperature dependence of spontaneous enthalpy-release and -absorption rates observed in the Na-RUB-18(wet) sample: gray circle, sample cooled rapidly at ca. 2 K min^{-1}; open circle, sample cooled slowly at ca. 20 mK min^{-1}.

peak in the heat capacity, and the temperature of 72 K corresponds just to that of phase transition due to the positional ordering of hydrogen atoms in the hydrogen-bond network of the bulk ice doped with a small amount of alkali hydroxide.[14,15] The glass-transition temperature, at which the relaxation time becomes 1 ks, of pure ice is known to be 105 K,[16] and the rearrangement of hydrogen atoms is frozen in below the temperature. Therefore, the configurational degree regarding the positions of the hydrogen atoms undergoes no phase transition due to their ordering at 72 K. However, the relaxation time decreases in the doped ice so that the phase transition at 72 K could be caused.[14] In the present wet sample, a small amount of sodium hydroxide was eliminated from the Na-RUB-18 crystal and is introduced into the extra bulk ice. Thus, the anomaly at 72 K originates from a phase transition, through which the hydrogen atoms in the hydrogen-bond network in ice become ordered, and the relaxation time of the rearrangement becomes 1 ks only below 72 K. In other words, the enthalpy-release/absorption anomaly around 100 K is not caused by a glass transition in the extra bulk ice included in the wet sample and therefore originates from the water between the silicate layers in Na-RUB-18. The anomaly around 240 K is due to the eutectic melting of bulk ice just as observed in the water solution[15] of 0.002 mol dm^{-3} NaOH without Na-RUB-18.

Here, one might think that the existence of eutectic melting of bulk ice around 240 K is inconsistent with the assumption in the present work that the heat capacity observed of the wet sample is given by the sum of the contributions from Na-RUB-18 and extra bulk ice/water. The quantity of sodium hydroxide associated with the eutectic melting was, however, small so that there should be no effect on the heat capacity values of ice and water except in the temperature ranges in which the melting proceeds. It has been confirmed that there is no difference observed in the temperature of 105–230 K and above 274 K between the heat capacities of the water solutions with and without a small amount of alkali hydroxide.[14,15] One might also think that part of the bulk ice does not undergo the phase transition at 72 K and shows a glass transition around 100 K. However, the decrease in the glass-transition temperature of the ice doped with alkali hydroxide is caused by the introduction of Bjerrum defects into the hydrogen-bond network.[17] The defects can move around over the whole network, whereas the doped hydroxide-ion sites are fixed within the network. In fact, only one glass transition has been found in HF-doped ice with T_g dependent on the HF concentration,[18] and no glass transition has been detected at around 100 K in ices doped with alkali hydroxide showing the 72 K phase transition.[14,15]

Filled and open circles in Fig. 5 represent the results of the samples cooled rapidly at 2 K min^{-1} and slowly at 20 mK min^{-1}, respectively, over the entire temperature range before the measurements. The former sample showed a spontaneous enthalpy-release effect, which started to appear at around 90 K, had a maximum at around 103 K, and turned into an absorption effect at around 110 K. The temperature drift then returned to a normal one at around 115 K. The latter sample, on the other hand, showed only spontaneous enthalpy-absorption effect, which appeared at around 95 K, had a maximum at around 106 K, and returned to normal behavior at 115 K. Such systematic dependence of the spontaneous enthalpy release/absorption on the pre-cooling rates of the sample can be attributed to a glass transition.[12,13] That is, when the sample is cooled rapidly to a low temperature in advance of the measurements, the configurational enthalpy of the sample is much greater than the equilibrium value at the glass-transition temperature T_g, and the sample releases heat to approach the equilibrium one on heating for the heat capacity measurements. On the other hand, when the sample is cooled slowly, the configurational enthalpy is much below the equilibrium value at the T_g, and the sample absorbs heat to approach the equilibrium on heating for the measurements. The T_g was estimated to be 106 K based on the empirical relation found hitherto.[12,13] A glass transition occurs as a freezing-in phenomenon of a classical rearrangement process, in which a molecule changes its position or orientation through surmounting a potential barrier $\Delta\varepsilon_a$. The relaxation time τ is generally expressed by an Arrhenius equation $\tau = \tau_0 \exp(\Delta\varepsilon_a/RT)$, where τ_0 is a pre-exponential factor in the range 10^{-13}–10^{-16} s corresponding to the frequency of translational or librational vibration of molecule.[19,20] Given $\tau_0 = 10^{-14}$ s, since $\tau = 10^3$ s at $T_g =$ 106 K, $\Delta\varepsilon_a$ of the frozen-in process was determined to be 34 kJ mol^{-1}.

Origins of the Phase Transition at 194 K and the Glass Transition at 106 K. Figure 6 shows the structural detail of the hydrogen-bond network composed of water molecules and silanol groups in Na-RUB-18 crystal. Figure 6a, as viewed along the *c* axis, illustrates schematically the hydrogen bonds, represented by gray bars, potentially formed in a water layer. The marks represent the same atoms/molecules as employed in Fig. 2. Sodium ions (gray circles) and water molecules represented by open circles are located on the same *ab* plane at the center of the water layer. Each of the water molecules (open circles) coordinates two sodium ions. On the other hand, water molecules represented by open squares are located just above and below the sodium ion on the plane and each mole-

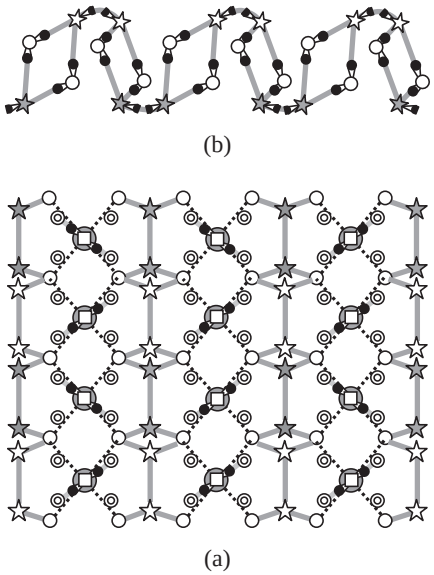

Fig. 6. Hydrogen-bond formation within a water layer (a) and the arrangement of water molecules and silanol groups in a one-dimensional hydrogen-bond network (b) in hydrated Na-RUB-18: double circle, siloxane-oxygen atom; open and gray star, silanol-oxygen atom; gray circle, sodium atom; open circle and square, water molecules coordinated to sodium ions; filled full-circle or half-circle, hydrogen atom; gray line, hydrogen bond; dotted line, coordination of the water molecule to the sodium ion. The orientation of the water molecules represented by open circles is determined uniquely. Each of the water molecules represented by open squares can form hydrogen bonds with siloxane-oxygen atoms and changes its orientation through ca. 90° rotation, which requires breaking two hydrogen-bonds, with respect to the C_2 molecular-symmetry axis.

cule coordinates one sodium ion. Therefore, the number of water molecules is the same between those represented by open circles and squares. Small black circles represent hydrogen atoms of water molecules. Open and gray stars stand for silanol-oxygen atoms located above and below, respectively, the plane. The water molecules represented by open circles and the silanol groups form a hydrogen-bond network in one dimension as shown in Fig. 6b. The two silanol-oxygen atoms forming a hydrogen-bond possess only one hydrogen atom. Consequently, both hydrogen atoms of each water molecule represented by open circle are located uniquely so that the water molecule forms hydrogen bonds with the two silanol-oxygen atoms having O(water)···O(silanol) distance of 0.281 nm. It is not clear whether the silanol-hydrogen atom at room temperature is disordered between two positions as represented by black half-circles in Fig. 6b or is located just on the midpoint between the two silanol-oxygen atoms. The one-dimensional hydrogen-bond network runs in the alternate directions between the *a* and *b* axes every layer along the *c* axis.

The water molecules represented by open squares in Fig. 6a are not bound so strongly at room temperature. They should form hydrogen bonds with siloxane-oxygen atoms represented by double circles and constituting each silicate layer; the O(water)···O(siloxane) distance is around 0.367 nm resulting in a rather weak hydrogen bond.[2] Here, it is noted that the activation energy for the rearrangement process responsible for the glass transition at $T_g = 106$ K was 34 kJ mol^{-1}. The magnitude corresponds roughly to the energy of two hydrogen bonds. Each water molecule represented by open square can change its orientation through rotation by ca. 90° with respect to the C_2 molecular-symmetry axis, and the rotation requires breaking two hydrogen bonds. It is noted further that the excess heat capacity due to phase transition at 194 K showed a wide skirt on the low-temperature side as well. In view that the reorientational degree of freedom can cause the phase transition, it is reasonable to assume that the glass transition occurred at the low temperature during complete ordering of the water molecules. This means that the contribution due to the degree of freedom to the heat capacity of the phase transition exists above and disappears below T_g.

Dashed line in Fig. 4 represents a baseline drawn for estimating the heat capacity of the phase transition. The excess part should appear to start at the T_g as described above and to be zero at room temperature at which the water molecules can even come out of and go into the crystal. Therefore, the baseline was drawn to link smoothly the heat capacities around 100 and 290 K. The open circles in Fig. 4 represent the excess heat capacities thus derived. The enthalpy and entropy of the transition were estimated to be 970 J (H$_2$O-mol)$^{-1}$ and 5.2 J K^{-1} (H$_2$O-mol)$^{-1}$, respectively. The entropy was 10.4 J K^{-1} (H$_2$O-mol)$^{-1}$ with respect only to the water molecules represented by open squares. According to the rearrangement model considered above, based on the T_g value and the feasible configurational degree of freedom, the number of permissible orientations of the water molecule is two at high temperatures; namely, the transition entropy is expected to be $R\ln 2$ (=5.76 J K^{-1} mol^{-1}). The present result is on the same order of magnitude, and the slightly large experimental value indicates that the water molecules on the high-temperature side of the transition temperature move with a large amplitude of vibration within and even to go out of the water layer. Therefore, the phase transition is interpreted as originating essentially from the orientational order/disorder of the water molecules indicated with open squares in Figs. 2 and 6, and the glass transition originating from the freezing-in of the reorientational motion.

Conclusion

There were two kinds of water molecules in Na-RUB-18. The ones represented by open circles in Figs. 2 and 6 were essentially ordered and link the silicate layers through hydrogen bonds with silanol-oxygen atoms. These bonds should be so strong that only the specified water molecules can be accommodated in the water layers. The water molecules, which form no hydrogen-bond network, were found to undergo a phase transition of an order–disorder type at 194 K with showing a wide heat-capacity skirt both on the low- and high-temperature sides and a glass transition at 106 K during the complete ordering in their orientations. The water molecules appeared to form rather strong hydrogen bonds with siloxane-oxygen atoms at low temperatures and rather weakly at room temperature such that they can be removed from the crystal. In other words, the water molecules gradually

approach the siloxane-oxygen atoms in their positions during orientational ordering with a decrease in the temperature. This property is potentially characteristic of water molecules in clays. The validity of this interpretation should be checked by further studies, such as using X-ray diffractometry below 194 K. The positional and motional states of silanol-hydrogen atoms also should be studied in detail.

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