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Swelling and dehydration characteristics of transition metal ion-exchanged taeniolites

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The swelling and dehydration characteristics of Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ion-substituted taeniolites with the exchange ratios of 85% and 78% have been investigated by high-temperature X-ray diffractometry, thermogravimetry–differential thermal analysis and calorimetry. The transition metal forms are the swelling states with two water-molecule layers at room temperature and a relative humidity of 70%, and their dehydration processes to the swelling states with a half water-molecule layer were concluded from the experimental results, to depend on the kind of the interlayer cations. In particular, the new swelling state with three-quarters water-molecule layers, showing a rational series of the basal reflections, was discovered to exist stably in the dehydration processes of manganese and nickel forms. The heat of swelling with water attains a maximum at a temperature corresponding to the appearance of the swelling state with a half water-molecule layer. The calorific value for the copper form was measured to be much larger than those for manganese, nickel and zinc forms.

1. Introduction

Lithium- and sodium-substituted taeniolites (LiT, $LiMg_2LiSi_4O_{10}F_2$ and NaT, $NaMg_2LiSi_4O_{10}F_2$), which are fluorine tetrasilicic micas, are swellable with water and exhibit different properties from nonswelling taeniolite (KT, $KMg_2LiSi_4O_{10}F_2$). Their basal spacings, dependent on the number of water-molecule layers around the interlayer cations, are drastically varied by swelling and dehydration. The swelling and dehydration characteristics of LiT and NaT were investigated by Kitajima and co-workers [1, 2]. As the interlayer cations in LiT and NaT are exchangeable, LiT and NaT are important for the preparation of various functional materials by the intercalation of inorganic and organic cations and molecules. The intercalation of amino acids to NaT was reported by Kitajima and Daimon [3]. Uematsu *et al.* [4] reported the different thermal properties of Fe^{3+} ion-exchanged LiT (Fe–LiT) from that of LiT and its catalysis. The transition metal ion-exchanged LiT and NaT were expected to be available for use as catalysts with interlayer acid sites. Therefore, it is of interest to investigate systematically the swelling and dehydration characteristics of the transition metal ion-exchanged LiT and NaT.

In the present paper, an extensive study of the swelling and dehydration characteristics of the divalent transition metal ion-exchanged LiT (Mn–, Ni–, Cu– and Zn–LiT) and NaT (Mn–, Ni–, Cu– and Zn–NaT) by means of high-temperature X-ray diffraction (XRD), thermogravimetry-differential thermal analysis (TG–DTA) and calorimetry, is reported.

2. Experimental procedure

LiT and NaT (Topy Ind. Co.) were used for preparation of the transition metal forms. Because LiT and NaT contained small amounts of α-cristobalite and other non-swelling portions as impurities, LiT and NaT were repeatedly washed with distilled water, and most of the impurities were removed by centrifugation prior to intercalation experiments. KT was synthesized using reagent-grade KF, LiF and SiO_2 as starting materials. The mixtures were carefully dried for 2 d at 130° C, melted in sealed platinum crucibles at 1400° C for 1 h, and cooled to 800° C at 2° C min^{-1}. The obtained sample was washed with distilled water to remove impurites. LiT, NaT and KT were dried at 80° C under vacuum and preserved in a desiccator with relative humidity (r.h.) of 70%. Characterization of the specimens was made by XRD (Shimazu XD-3).

Cation-exchange reaction experiments were conducted as follows: each 200 mg specimen was allowed to react with 200 ml 0.01 M chloride solutions containing Mn^{2+}, Ni^{2+}, Cu^{2+} or Zn^{2+} ions with stirring at 25° C. After the reaction, the solid and solution phases were separated by centrifugation. Part of supernatant liquid was collected and analysed for lithium, sodium, nickel, manganese, copper and zinc by atomic absorption spectroscopy (Hitachi 180-30) and cholate titration method using EDTA (Ethylenediamietetracetic acid disodium salt). The solid samples were washed repeatedly with distilled water, dried at 80° C under vacuum, and stored in the desiccator as above.

The dehydration characteristics of the obtained transition metal forms in air were determined using

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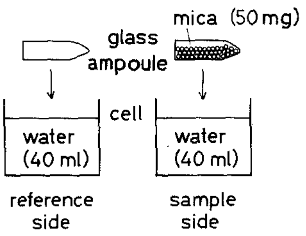

Figure 1 Schematic diagram of the measurement system.

XRD equipped with an electric furnace (Rigaku RAD-IIC) and TG–DTA (Rigaku TG–DTA) with α-Al_2O_3 as the reference material up to 500° C. The swelling characteristics with water were examined by calorimetry as is schematically represented in Fig. 1. A glass ampoule containing a 50 mg sample from the desiccator was heated at various temperatures up to 400° C for 1 h and sealed . The sample and empty ampoules were placed in the two cells of the twin condution-type microcalorimeter (Tokyo Riko MPC-11), together with 40 ml distilled water until thermal equilibrium at 25 ± 0.1° C was reached. Then both ampoules were broken in the water at the same time in order to cancel out the heat of destruction of glass ampoules, and the heat liberated was recorded. The heat value of swelling was calculated using the reference heat measured in advance. Each datum obtained was actually the average of at least three measurements for each sample.

3. Results and discussion

3.1. Identification of the specimen

The synthetic sample was identified as KT with a basal spacing of 0.99 nm by XRD. Both LiT and NaT with a basal spacing of 1.23 nm were also confirmed to be swelling states with one water-molecule layer (d_1) at room temperature and r.h. = 70% and contained no impurities. The interlayer Li^+ and Na^+ ions were estimated to be surrounded by three and two water molecules, respectively, in the d_1 from the TG–DTA analyses. The estimated value for LiT is large compared with Hendricks' model [5] and the previous results [1, 2], while that of NaT is in good agreement with them.

3.2. Cation exchange

The uptake of Ni^{2+} ions by LiT, NaT and KT as a function of time is shown in Fig 2. The intercalation reactions of Ni^{2+} ions easily occurred in LiT and NaT and almost attained equilibria within 1 and 6 h for LiT and NaT, respectively, although equilibrium was not reached in KT at all. The molar ratio between interlayer cations released from LiT or NaT and Ni^{2+} removed from the solution was found to be $Li^+/Ni^{2+} \simeq 2.0$. The interlayer cations of about 85% and 78% in the d_1 of LiT and NaT, whose theoretical exchange capacities for divalent cations are 1.35×10^{-3} and 1.28×10^{-3} mol g^{-1}, were exchanged with Ni^{2+} ions at an equilibrium state, respectively.

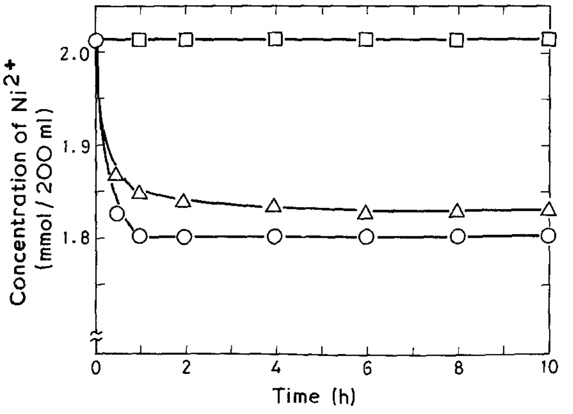

Figure 2 Uptakes of Ni^{2+} ions by LiT, NaT and KT at 25° C as a function of time. (○) LiT, (△) NaT, (□) KT.

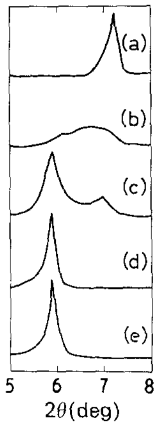

Figure 3 X-ray diffractograms of Ni^{2+} ions-exchanged LiT as a function of exchange ratio. (a) 0%, (b) 15%, (c) 30%, (d) 50%, (e) 85%.

Similar amounts of interlayer cations in d_1 of LiT and NaT, as the case of Ni^{2+} ions, were exchanged with Mn^{2+}, Cu^{2+} and Zn^{2+} ions in the solutions. Consequently, it was found that the cation-exchange reactivity relied on the degree of the swelling, and LiT and NaT did not show ion-selectivity for transition metal ions.

The influence of the residual interlayer Li^+ or Na^+ ions on the hydrated states was examined, because all the interlayer cations could not be exchanged with the transition metal ions in the solution at 25° C. The X-ray diffractograms of Ni^{2+} ion-exchanged LiT as a function of exchange ratio are shown in Fig. 3. The peak at $2\theta \simeq 7.2°$ from LiT became broadened and its position shifted towards lower diffraction angles at the exchange ratio of 15%. This suggests the transformation to an irregular interstratified structure of LiT and Ni–LiT. Then, the peak at $2\theta \simeq 5.9°$ from Ni–LiT was strengthened with increasing exchange ratio, and the irregular interstratified structure changed to a mixture of LiT and Ni–LiT at the exchange ratio of 30%. The peak from LiT finally disappeared above an exchange rate of 50%. Similar aspects were observed in other transition metal forms with different exchange ratios. The results from XRD were consistent with those from TG–DTA. Therefore, it was concluded that the influence of the residual interlayer Li^+ or Na^+ ions on the swelling and dehydration characteristics of the transition metal forms with an exchange ratio of 85% or 78% were negligible.

3.3. High-temperature XRD

The basal spacings of all the transition metal forms in the present study were measured to be 1.51 nm at

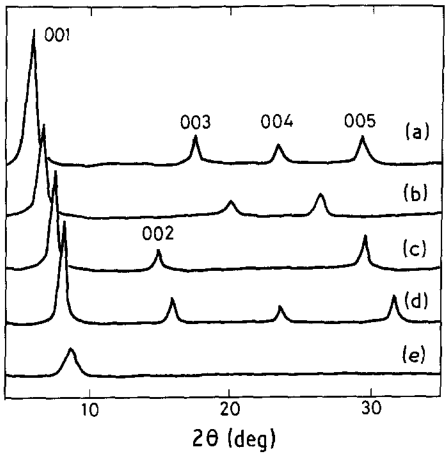

Figure 4 X-ray diffractograms of Ni–LiT as a function of temperature. (a) Room temperature, (b) 70° C, (c) 115° C, (d) 130° C, (e) 270° C.

room temperature and r.h. = 70%. These values are close to those of LiT and transition metal forms with two water-molecule layers (d_2) reported by previous papers [1, 6]. The swelling states of the transition metal forms were sensitive to humidity.

The X-ray diffractograms of Ni–LiT as a function of temperature are shown in Fig. 4. The peak positions of basal reflections shifted stepwise towards higher diffraction angles with increasing temperature. Finally, the basal reflections, except for the broadened 0 0 1 reflection, were undetectable above 260° C. The temperature dependence of the measured basal spacing for Ni–LiT is shown in Fig. 5. The basal spacing decreased stepwise from 1.51 to 1.38 nm at about 70° C, to 1.22 nm at about 110° C, to 1.14 nm at about 130° C, and to 1.03 nm at about 260° C. After that, the Ni–LiT skeleton gradually collapsed with dehydration to the anhydrous state (d_0). The contraction of the basal spacing is ascribed to the leakage of water molecules coordinated around interlayer Ni^{2+} ions by heating. Referring to the previous paper on LiT [1], the basal spacings of Ni–LiT at about 70, 110 and 260° C were assigned as corresponding to the swelling states with three-halves water-molecule layers ($d_{3/2}$), one water-molecule layer (d_1), and one-half water-molecule layer ($d_{1/2}$), respectively. $d_{3/2}$ and d_1 showed rational series of basal reflections. The swelling state, however, which discontinuously appeared at about 130° C and stably lasted up to about 250° C, could not be divided into the usual classes of the hydrated types. This phase was considered to be an ordered layer structure, because of the rational series, namely $d(0\,0\,1) = 1.15$, $d(0\,0\,2) = 0.57$, $d(0\,0\,3) = 0.38$ and $d(0\,0\,4) = 0.28$ nm, as well as the sharpness of the basal reflections. The clearance space as the difference between the basal spacings at room temperature and at 130° C, was estimated to be 1.32 times as large as the dimension of one water molecule, assumed to be 0.28 nm. The swelling state of this new phase was therefore named the three-quarters water-molecule layer ($d_{3/4}$). d_1 with the basal spacing of 1.22 nm emerged at a transitional period from the $d_{3/2}$ to $d_{3/4}$. The clearance space as the difference between d_2 and d_1 is in good agreement with the dimension of one water molecule. As the $d_{3/2}$, $d_{3/4}$ and $d_{1/2}$ are hardly interpreted by Hendricks' model [5], the water molecules were considered not to be all on the same plane, but some of them were to be located in the SiO_4 tetrahedral sheet.

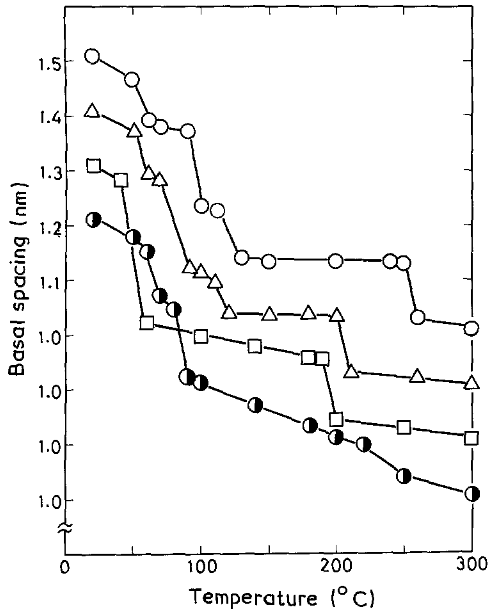

Figure 5 Basal spacings of transition metal forms as a function of temperature. (○) Ni–LiT, (△) Mn–LiT, (□) Cu–LiT, (◑) Zn–LiT.

The temperature dependences of the basal spacings of Mn–, Cu– and Zn–LiT are also shown in Fig. 5. d_2 of Mn–LiT was transformed to d_1 with a basal spacing of 1.22 nm via $d_{3/2}$ at about 95° C. The appearance of $d_{3/2}$ with a basal spacing of 1.38 nm corresponds to the endothermic shoulder on the DTA curve at about 65° C as is seen in Fig. 6. Then d_1 was transformed to $d_{3/4}$ with a basal spacing of 1.14 nm at about 120° C and to $d_{1/2}$ with a basal spacing of 1.03 nm at about 210° C. $d_{3/4}$ of Mn–LiT was as stable as that of Ni–LiT, showing a rational series of basal reflections.

d_2 of Cu–LiT was transformed to d_1 with a basal spacing of 1.22 nm at about 60° C. The basal spacing of d_1 gradually shrank with increasing temperature, and then jumped to 1.04 nm at about 200° C. The discontinuous decrease of the basal spacing is the transformation to $d_{1/2}$. Stable $d_{3/2}$ and $d_{3/4}$ could not be found in the dehydration process of Cu–LiT.

d_2 of Zn–LiT was transformed to $d_{3/2}$ with a basal spacing of 1.37 nm at about 70° C and to d_1 with a

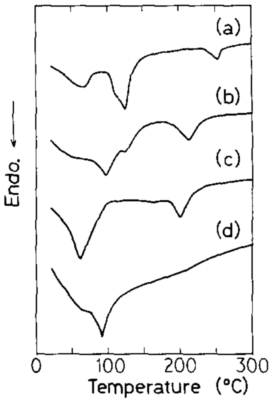

Figure 6 DTA curves for transition metal forms. (a) Ni–LiT, (b) Mn–LiT, (c) Cu–LiT, (d) Zn–LiT.

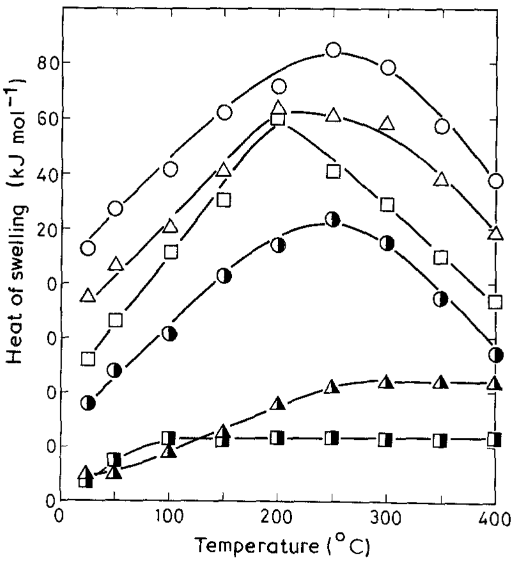

Figure 7 Heats of swelling with water per interlayer cation as a function of treatment temperature. (○) Ni–LiT, (△) Mn–LiT, (□) Cu–LiT, (◑) Zn–LiT, (▲) LiT, (◨) NaT.

basal spacing of 1.22 nm at about 90° C. The basal spacing gradually decreased with increasing temperature, and d_1 changed to $d_{1/2}$ whose basal spacing is 1.04 nm at 250° C. $d_{3/4}$ of Zn–LiT did not appear in a stable form, and the discontinuous transformation to $d_{1/2}$ could not be clearly observed. This is consistent with the fact that there was no distinct endothermic peak above 100° C on the DTA curve of Zn–LiT, as seen in Fig. 6.

Ni–, Mn–, Cu– and Zn–NaT exhibited the same dehydration processes as Ni–, Mn–, Cu– and Zn–LiT, respectively. From these results, it was concluded that the dehydration characteristics of the transition metal forms depend on the type of interlayer cations.

3.4. TG–DTA

The DTA and TG curves of the transition metal forms revealed the endothermic peaks and stepwise weight loss at temperatures corresponding to discontinuous changes of the basal spacings. The total weight losses due to dehydration from d_2 to $d_{1/2}$ were 15.2%, 15.1%, 16.8% and 14.7% for Ni–, Mn–, Cu– and Zn–LiT, respectively. Thus, Ni^{2+}, Mn^{2+} and Zn^{2+} ions were estimated to be surrounded by 10 water molecules in d_2, while Cu^{2+} ions are surrounded by 12 water molecules. Similar results were obtained from the total weight losses of Ni–, Mn–, Cu–, and Zn–NaT.

3.5. Heat of swelling

The swelling of taeniolites in water was an exothermic reaction, and the measured heats of swelling were converted per interlayer cation. Fig. 7 shows the heats of swelling for the transition metal forms as a function of treatment temperature, together with those for LiT and NaT. The heats of swelling for Ni^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+} increased with increasing temperature and attained maxima of 85, 84, 102 and 84 kJ mol^{-1}, respectively, in the temperature range 200 to 250° C, where $d_{1/2}$ appears in stable form. On the other hand, those for LiT and NaT attained constants of 43 and 23 kJ mol^{-1} above 250 and 100° C, where $d_{1/2}$ and d_0 are stable, respectively. The order of the heat of swelling was found to be proportional to the order of the number of water molecules around the interlayer cation in the same swelling state. A decrease in the heat of swelling in the transition metal form suggests the absence of reversible swelling and dehydration characteristics on collapse of the taeniolite structure.

TABLE I Calorific values for forming each swelling state per interlayer cation in transition metal forms

	Heat of formation (kJ mol^{-1})		
	$d_{1/2} \rightarrow d_1$	$d_1 \rightarrow d_2$	$d_2 \rightarrow d_3$
Ni–LiT	43	30	13
Mn–LiT	43	28	13
Cu–LiT	75	14	12
Zn–LiT	41	28	15

The heats of formation of each swelling state estimated from the results of high-temperature XRD and calorimetry are listed in Table I. The order of the calorific values (i.e. the strength of the bond to the interlayer cation) was found to be $d_{1/2} \rightarrow d_1 > d_1 \rightarrow d_2 > d_2 \rightarrow d_3$, where d_3, is the maximum swelling state with three water molecule layers for the transition metal form. In particular, the heat for $d_{1/2} \rightarrow d_1$ is considerably larger and that for $d_1 \rightarrow d_2$ is smaller in Cu–LiT, compared with those in Ni–, Mn– and Zn–LiT. This was considered to be due to the distortion of the polyhedron around the Cu^{2+} ion by the Jahn–Teller effect.

4. Conclusion

The swelling and dehydration characteristics of Mn^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} ion-exchanged LiT and NaT have been investigated by high-temperature XRD, TG–DTA and calorimetry. It was found that, 85% and 78% of the interlayer cations in d_1 of LiT and NaT, respectively, are easily exchanged with the transition metal ions in the solution; however, those in KT are not exchanged. The influence of residual interlayer cations on the swelling states of the transition metal forms with higher exchange ratio was negligible.

The swelling states of the transition metal forms are d_2 at room temperature and r.h. = 70%, in which Ni^{2+}, Mn^{2+} and Zn^{2+} are surrounded by 10 water molecules while Cu^{2+} are surrounded by 12 water molecules. The dehydration characteristics of the transition metal forms depend on the kind of interlayer cations produced by heating. Namely, d_2 of Ni–LiT is transformed to $d_{3/2}$ at about 70° C, to d_1 at about 110° C, to the newly discovered $d_{3/4}$ at about 130° C, and to $d_{1/2}$ at about 260° C. d_2 of Mn–LiT is transformed to $d_{3/2}$ at about 65° C, to d_1 at about 95° C, to $d_{3/4}$ at about 120° C, and to $d_{1/2}$ at about 210° C. d_2 of Cu–LiT is transformed to d_1 at about 60° C and to $d_{1/2}$ at about 200° C. d_2 of Zn–LiT is transformed to $d_{3/2}$ at about 70° C, to d_1 at about 90° C, and gradually to $d_{1/2}$ around 250° C. The taeniolite structure collapses on dehydration to d_0, and the reversible swelling and dehydration characteristics disappear.

The measured heat of swelling with water reaches a maximum at a temperature corresponding to the stable appearance of $d_{1/2}$. The order of the calorific values is Ni–LiT = Mn–LiT = Zn–LiT < Cu–LiT, and the Jahn–Teller effect was observed in Cu–LiT. Mn–, Ni–, Cu– and Zn–NaT show the same swelling and dehydration characteristics as Mn–, Ni–, Cu– and Zn–LiT, respectively.

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