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Local Structure of the Interlayer Ion in Synthetic Fluorine Mica

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Abstract: Na-form tetrasilicic fluorine micas, *i.e.*, sodium taeniolite (NaT , $\text{NaMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$) and sodium hectorite (NaH , $\text{Na}_{1/3}\text{Mg}_{8/3}\text{Li}_{1/3}\text{Si}_4\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$), exchanges their Na^+ , the interlayer cation, for K^+ , Rb^+ , Ca^{2+} , Ni^{2+} , and other cations in solutions. NaT shows remarkably high selectivity for K^+ , Rb^+ , and Cs^+ and NaH does for Rb^+ and Cs^+ . XAFS of the exchanged ions in NaT and NaH were analyzed and powder X-ray diffractions were measured to investigate the layer stacking. Characteristics of ion-exchange selectivity of these micas were revealed by the local structure of the interlayer ion. Rb K-edge EXAFS of all samples show slightly longer Rb– O_{1st} distance than K– O_{1st} in taeniolite (its original anhydrous K-form). It indicates that Rb^+ for the micas is exchanged as an anhydrous state. X-Ray diffraction patterns showed hydrated interlayer-ion phases at low-exchanged NaT and NaH. The hydrated phases decreased with increasing the exchange ratio and then less-hydrous Rb-phase increased. Although Cs^+ -exchanged NaT show only an anhydrous state in XAFS, Sr^{2+} and Ba^{2+} in NaT was hydrous as if in aqueous solution.

1. INTRODUCTION

Inorganic ion exchangers have their specific ion-selectivity to exchange reaction. Na-form taeniolite (NaT , $\text{NaMg}_2\text{LiSi}_4\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$) exchanges its Na^+ , the interlayer cation, for K^+ , Rb^+ , NH_4^+ , etc. in solutions. Na-form hectorite (NaH , $\text{Na}_{1/3}\text{Mg}_{8/3}\text{Li}_{1/3}\text{Si}_4\text{O}_{10}\text{F}_2 \cdot n\text{H}_2\text{O}$) exchanges for Rb^+ , Cs^+ , and other cations. NaT shows especially high selectivity for K^+ , Rb^+ , Cs^+ , and NH_4^+ , and NaH does for Rb^+ and Cs^+ . According to diffraction, reaction heat, and thermal gravimetric studies, it is anticipated that the local structure of the exchanged ions affects the selectivity for ion-exchange reactions. In this study, NaT and NaH were exchanged for Rb^+ , Cs^+ , and other cations. The structural changes were studied by XAFS of the exchanged ion and powder X-ray diffraction patterns to reveal the relation of their ion-exchange selectivity and the local structure around the interlayer ions.

2. EXPERIMENTAL

Commercially available fluorine micas were used after removing impurities such as SiO_2 (*tetra*) or starting materials by washing with water followed by separation with centrifugation. Rubidium, caesium, strontium, and barium chloride solutions were used for the reactions under 25°C . Exchange ratios of Rb^+ to Na^+ in the micas were varied from 0.5% to the maximum. For another cations, exchange ratios were 40% and 55%. X-Ray absorption spectra of Rb and Sr K-edge and Cs and Ba L_{III}-edge were obtained at BL-10B and BL-7C in the Photon Factory of the National Laboratory for High Energy Physics. EXAFS Fourier transforms were performed according to the procedures in the reference [1]. X-Ray powder diffraction patterns were measured by Rigaku RINT Ultima⁺. Rb- and Cs-exchanged NaT or NaH were prepared to be wet with the exchange reaction solution or deionized water, respectively, for both measurements, because they show structural changes in X-ray diffraction with drying.

Figure 1. XANES spectra of ion-exchanged NaT (solid lines) and nitrate or chloride aqueous solution (broken lines).

3. RESULTS AND DISCUSSION

Figure 1 shows XANES spectra of Rb and Sr K-edge and Cs and Ba L_{III}-edge uptaken into NaT and their 0.1 mol/dm³ nitrate or chloride solutions. XANES of Rb- and Cs-exchanged NaT are apparently different from those of aqueous solution whereas those of Sr- and Ba-exchanged ones are similar. It shows that Rb and Cs take another local structure than in the solution state. The exchanged NaT of all exchange ratio for each exchange ion showed identical XANES spectra. EXAFS Fourier transforms of exchanged NaT are shown in Fig. 2. There is a large peak at the identical position with that in aqueous solution in the transform of Sr and Ba-exchanged NaT. These cations are hydrated as if in aqueous solutions. Rb and Cs-exchanged NaT show many peaks in the transform. According to the crystal structure of K-type taeniolite, KMg₂LiSi₄O₁₀F₂ [2], these peaks can be assigned as Fig. 2 (a) indicates. Rb-exchanged NaT show no peak or shoulder for the hydrated water oxygen at the position for aqueous solution. After drying at 500°C, the maximum Rb-exchanged NaT also shows the same characters to Figs. 1 and 2. These alkaline cations are held as an anhydrous form.

X-Ray diffraction patterns around basal plane reflection, i.e., (001) diffraction of 1M-type mica, of NaT and NaH after Rb-exchange reaction for the low and the high exchange ratios are shown in Fig. 3. NaT show two- ($2\theta \sim 5.8^\circ$), one- (7.4°), or no-water layer (9.2°) phase of Na-form taeniolite and anhydrous Rb-form phase (8.7°) owing to their exchange ratio. NaH gives only Rb-form hectorite phase with two- ($2\theta \sim 5.7^\circ$), one- (6.9°), or no-water (8.6°) layers. In both micas, the two-water layers decrease with increasing the ratio, the less-hydrous layers increase instead. From the diffraction pattern changes with the exchange ratios, the layers of the micas containing water can exchange its Na⁺ and they become an anhydrous form.

Figure 3. X-Ray diffraction patterns of Rb-exchanged NaT and NaH. Exchange ratios are low (solid lines) and the maximum (broken lines).

Figure 4. Rb K-edge XANES spectra of Rb-exchanged NaH. Solid and broken lines show low and high exchange ratios, respectively.

Figure 5. EXAFS Fourier transforms of Rb-exchanged NaH. Phase shift is corrected as Rb-O. Solid and broken lines show low and high exchange ratios, respectively.

From the information of XAFS and powder diffractions, a following mechanism of Rb-exchange reaction in NaT can be depicted. At the first stage, Na⁺ in a two-water layer is exchanged for Rb⁺. In this exchange reaction, Rb⁺ detaches its hydration waters. When the ratio of Rb⁺ in the two-water layer reaches at a certain critical value, the layer begins excluding its interlayer waters until it become an anhydrous form. Finally, all the layers in a sample become anhydrous forms and then the whole exchange reaction stops.

Figure 4 shows XANES spectra of Rb K-edge uptaken into NaH. It shows that Rb takes another local structure than in the solution state. XANES for NaH of low exchange ratios were the same as NaT, but those of the high ratios become somewhat similar to that for the aqueous solution. EXAFS Fourier transforms of exchanged NaH are shown in Fig. 5. When the exchange ratio is low, there is only small shoulder for the hydrated water oxygen at the position (about 2.8 Å) for the aqueous solution. Therefore, most of Rb⁺ is placed as the anhydrous form in NaH at low exchange ratio. Hydrated Rb⁺ in NaH increases with increasing the exchange ratio.

The diffraction pattern changes of NaH accord with those of NaT except the species of the interlayer cation. But, it is not consistent with the XAFS results. This inconsistency may be come from the difference of selectivity of the two methods. At the low exchange ratio, most of the Rb-containing layers of NaH are anhydrous but would be spread randomly in the sample. Therefore, there is no diffraction peak at $2\theta \sim 8.6^\circ$ at low exchange ratios.

References

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