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The Ion-Exchange Property of Some Layered Inorganic Materials with Potassium Ion, Rubidium Ion and Cesium Ion, and Selective Cesium Ion-Exchange of Synthetic Mica

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The ion-exchange property of sodium difluorotetrasilicate, Na-TSM, with potassium, rubidium and cesium ions was investigated in addition to two other typical layered inorganic materials. The selectivity sequence of Na-TSM was $Cs^+ > Rb^+ > K^+$ and the selectivity difference of Na-TSM was highest among the examined layered materials. It was found from a chemical analysis that cesium ion-exchange participated in magnesium ions, which is a lattice component of Na-TSM, in addition to an ordinary ion-exchange reaction with the interlayer sodium ions. The exchange of cesium ions with magnesium ions was found to be stoichiometric, and was expected to be an ideal ion-exchange reaction. It was a peculiar phenomenon only on Na-TSM. Once cesium ions were exchanged in a Na-TSM lattice, they were hardly released, due to a reverse ion-exchange with sodium ions. The highest selectivity difference and tight binding of cesium ions were interpreted by an ion-exchange with lattice magnesium ion as well as decreased dehydration, which resulted in the interlayer gallery height.

Nuclear electric-power generation and nuclear tests have emitted a large amount of ^{137}Cs, which β-decays to ^{137}Ba, involving γ-decay. Because of the rather long half-life of ^{137}Cs (30.2 y), it causes a serious environmental pollution problem. The development of new materials to remove ^{137}Cs selectively from nuclear waste has been expected, especially in Japan, which obtains 33% of its electric power from nuclear electric-power generation. In the future, closed nuclear reactors in which very long-life radioisotopes are quenched and the final main radioactive product is ^{137}Cs will be built.[1] Inorganic ion exchangers are one of the promising materials for the stratum disposal of ^{137}Cs, because they have a higher selectivity difference among similar ions than the organic resins without any special treatment, such as chelation.[2—4]

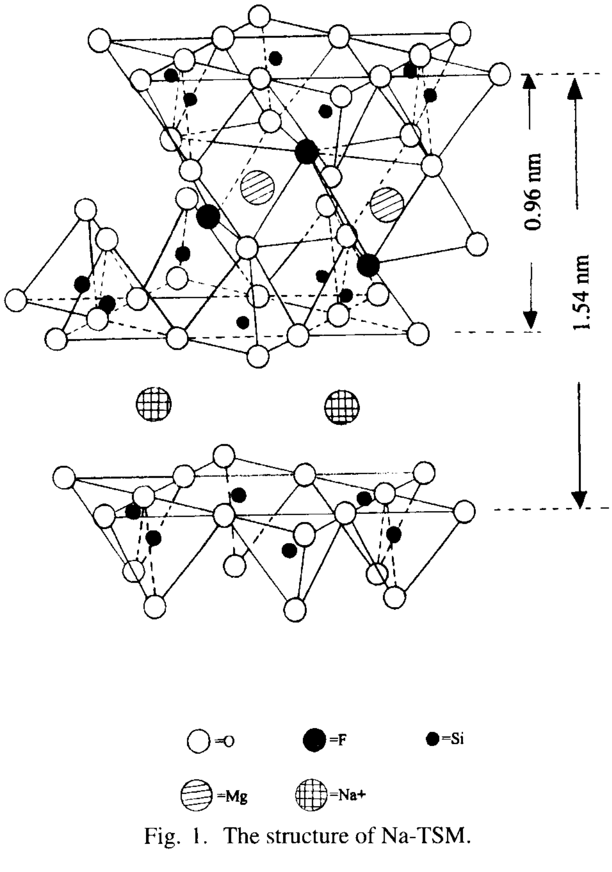

Fig. 1. The structure of Na-TSM.

Most of the layered inorganic materials contain cation-exchange sites between the layered lamellae, which are made of a negatively charged framework. Among them, synthetic mica has peculiar properties for alkali metal ions. For example, sodium difluorotetrasilicate ($Na[Mg_{2.5}Si_4O_{10}F_2]\cdot 2H_2O$: sodium-type tetrafluorosilicic mica,[5] Na-TSM) and potassium difluorotetrasilicate ($K[Mg_{2.5}Si_4O_{10}F_2]$: potassium-type tetrafluorosilicic mica, K-TSM) have entirely different characteristics. The former has an interlayer gallery height of about 0.6 nm (Fig. 1), corresponding a *c*-lattice parameter of 1.5 nm and includes hydrated interlayer sodium ions. The hydrating water molecules were found to have a bi-layer form.[6] Because of the large interlayer spacing, Na-TSM can easily form various intercalation compounds, since the interlayer spacing is very stretchable. The expansion reaches about 6 nm in the case of phospholipid intercalation.[7] On the other hand, K-TSM has a small interlayer gallery height, almost the size of the anhydrated potassium ion radius. In fact, the interlayer potassium ions are not hydrated in a manner consistent with its chemical formula.[5] It has a strong bonding between lamellae and so the intercalation as well as the ion-exchange reaction hardly occurs. These peculiar properties of TSMs against monovalent ions may result in some specific ion-exchange selectivity on the cesium ions.

This paper reports on the general ion-exchange property of Na-TSM with potassium, rubidium and cesium ions in comparison with the ion-exchange property of lithium hectorite and sodium taeniolite. The selective cesium ion-exchange mechanism of Na-TSM is interpreted according to the exchange with magnesium ions as well as shrinking of the interlayer gallery height.

Materials and Method

Materials. Synthetic layered materials (sodium tetrafluorosilicic mica ($Na[Mg_{2.5}Si_4O_{10}F_2]\cdot 2H_2O$: Na-TSM), lithium hectorite ($Li_{1/3}Mg_{8/3}Li_{1/3}(Si_4O_{10})F_2\cdot nH_2O$) and sodium taeniolite ($NaMg_2Li(Si_4O_{10})F_2\cdot nH_2O$)) were supplied from Topy Industry Co. Ltd., Japan.

Preparation of Na^+, K^+, Rb^+, and Cs^+ Solutions. Solutions of sodium, potassium, rubidium and cesium ions were prepared from reagent-grade sodium chloride, potassium chloride, rubidium chloride (Kanto Chemical Co., Inc.) and cesium chloride (Wako Pure Chemical Industries, Ltd.), respectively. Ultrapure water (specific resistance was 17 MΩ·cm : PURIC system, (Japan Organo Co., Ltd.)) was used to prepare alkali metal solutions.

Preparation of Layered Materials. The supplied 10% Na-TSM sol was washed with ultrapure water several times, and a precipitated powder was filtered and air-dried.[7] Other layered materials supplied in the powdered form were used without further purification.

Characterization. A powder X-ray diffractometer (MO3X-HF, MAC Science Co., Ltd., Japan) equipped with mono-chromized Cr-$K\alpha$ and Cu-$K\alpha$ radiations, $\lambda = 0.2896$ nm and $\lambda = 0.1541$ nm, respectively, was used to characterize the layered materials before and after the ion-exchange reaction.

Analysis. An atomic absorption spectrophotometer, abbreviated as AAS (HITACHI 170-30, Hitachi, Ltd.), was used to determine alkali metal ions. An inductively coupled plasma atomic emission spectrometer, abbreviated as ICP (SHIMADZU ICPS-5000, Shimadzu Corp.), was used to determine magnesium ions.

Distribution Coefficient (K_d). The K_d values of the ion-exchange reaction with potassium, rubidium and cesium ions were determined as follows: 0.2 g of layered materials (about 5×10^{-4} mol) was immersed in a 20 cm^3 of the solution containing 0.01 mol dm^{-3}, 0.003 mol dm^{-3} and 0.001 mol dm^{-3} of each alkali metal ions at 60 °C for 48 h. After equilibration, a supernatant solution was filtered through a 0.8 μm micro disk; the amount of metal ions which remained or were released in the supernatant solution was then determined by AAS or ICP. Polypropylene containers were used to avoid contamination due to sodium ions from the glass vessel. The amount of metal ions sorbed in the exchanger phase was estimated from the difference between the initial and final concentrations in the supernatant solution. The K_d values were calculated using

$$K_d = \frac{\text{Mole of metal ions in exchanger}}{\text{Mole of metal ions in solution}} \times \frac{\text{volume of solution (cm}^3)}{\text{mass of exchanger (g)}}.$$

Reverse Ion-Exchange. A reverse ion-exchange study was carried out to estimate the fixation ability of cesium ions. Layered materials which had been ion-exchanged in 0.003 mol dm^{-3} cesium ion solution in advance were used. Then, a cesium ion-exchanged sample was immersed in a 0.01 mol dm^{-3} sodium chloride solution. The suspension was allowed to react at 60 °C for 48 h. The concentrations of cesium ions and magnesium ions which were released into the supernatant solution were determined.

Results and Discussion

Ion-Exchange Selectivity. The alkali metal ion-exchange property of Na-TSM, Na-taeniolite and Li-hectorite was surveyed in order to reveal the cesium ion selectivity of Na-TSM. Plots of $\log K_d$ vs. $\log [M^+]$ are shown in Figs. 2a, 2b, and 2C. No significant ion-exchange selectivity difference was observed on Na-taeniolite among the three kinds of alkali metal ions examined. Li-hectorite had a slight selectivity difference between rubidium and cesium ions at low concentrations. In contrast, the selectivity difference among three kinds of alkali metal ions was remarkable on Na-TSM, especially at low concentrations, and the selectivity sequence was $Cs^+ > Rb^+ > K^+$.

Cs^+ Selectivity among Layered Materials. The K_d value for cesium ions was estimated on three different layered materials at a similar concentration of 0.01 mol dm^{-3} from Fig. 2. It was found that Na-taeonilite had excellent selectivity for cesium ions among the examined layered materials.

Reverse Ion-Exchange. The reverse ion-exchange of cesium ion-exchanged Na-TSM with sodium ions was examined in order to reveal the tight binding of cesium ions in the Na-TSM lattice. The amount of released cesium ions was below the detection limit. This result indicated that the exchanged cesium ions were tightly fixed in the exchanger's phase, suggesting that Na-TSM is a promising material for the stratum disposal of ^{137}Cs. The peculiar ion-exchange mechanism of cesium ions is discussed below based on a chemical analysis (stoichiometry) and an X-ray diffraction analysis.

Powder X-ray Diffraction Study. Figures 3a, 3b, 3c, 3d, and 3e show the powder X-ray diffraction patterns of Na-TSM before and after ion-exchange with potassium, rubidium and cesium ions and as-supplied K-TSM, respectively. From these patterns, the arrangements of hydrated water molecules between lamellae can be known. Generally speaking, the gallery height of the interlayer changes stepwise, reflecting the arrangement of water molecules: the bilayer form, the monolayer form and the anhydrous form,[9,10] if no specific bonding is formed between the hydrated ions and the layered lattice, such as covalent bonding. Although the hydration behaviors of potassium ions, rubidium ions, and cesium ions are similar in the interlayer gallery of ordinary mica minerals, reflecting the hydration property in aqueous solution,[10] a peculiar property is observed only on Na-TSM. Na-TSM is the only mica mineral in which cesium ions are accommodated in the anhydrous form during an ion-exchange reaction in an aqueous solution, resulting in a narrow d-spacing of about 1.0 nm. Na-TSM was found to

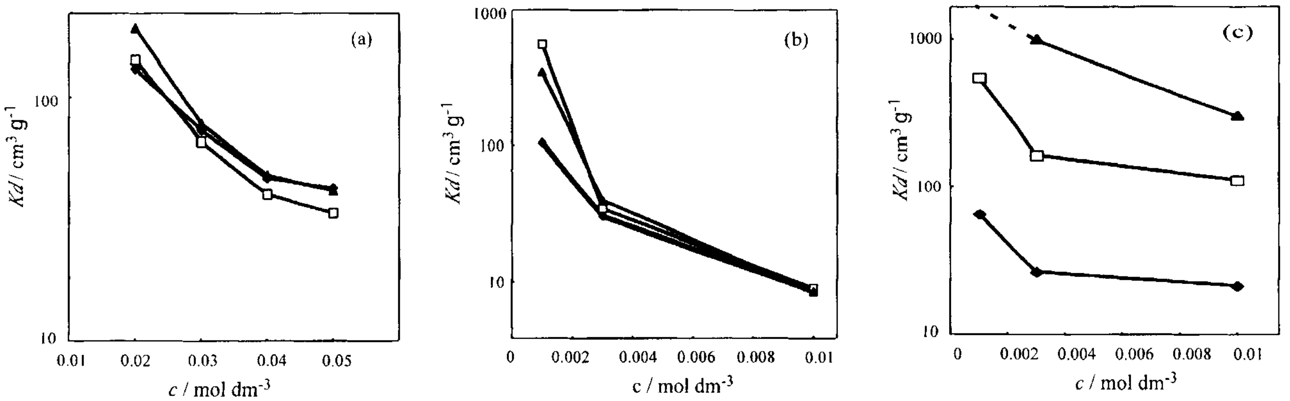

Fig. 2. K_d values of alkali metal ions on layered materials. a: Na-taeniolite, b: Li-hectorite, c: Na-TSM. Exchanger: 0.2 g, Volume: 20 cm^3, Solution : KCl, RbCl, CsCl. ◆:K^+, □:Rb^+, ▲:Cs^+.

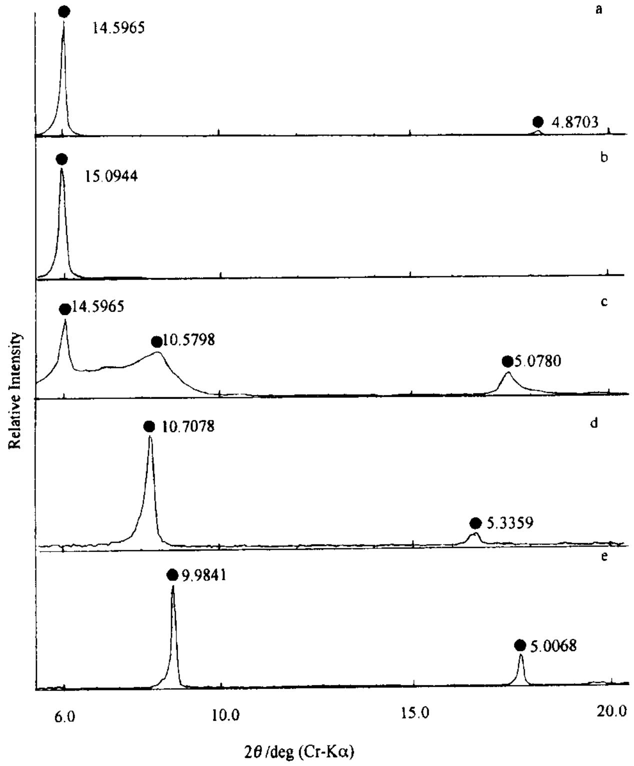

Fig. 3. Powder X-ray diffraction patterns. a: Na-TSM, b: Na-TSM after the ion exchange with K^+, c: Na-TSM after the ion exchange with Rb^+, d: Na-TSM after the ion exchange with Cs^+, e: as-supplied K-TSM.

have d-spacings of about 1.5, 1.25 and 1.0 nm for the bilayer, the monolayer and the anhydrous form, respectively. The d-spacings before and after potassium ion-exchange were 1.46 and 1.51 nm, respectively (Figs. 3a and 3b). Thus, it was concluded that Na-TSM after ion-exchange with potassium ions has a bilayer form of water molecules. This result indicated an insufficient exchange (low K_d value) of sodium ions with potassium ions. The residual sodium ions determined the bilayer form[11] to be superior to the potassium ions, which have a weak hydrating ability. On the other hand, a rubidium ion-exchanged sample showed mixed phases: one had a bilayer form and the other an anhydrous form, each having d-spacings of 1.46 and 1.06 nm, respectively (Fig. 3c). Na-TSM after ion-exchange with cesium ions had the structure of an anhydrated state; the d-spacing was 1.07 nm (Fig. 3d). The dehydration and the following tight fixation of cesium ions on Na-TSM may be ascribed to the strong shrinkage of the gallery height and the formation of an anhydrated state similar to the as-supplied K-TSM (Fig. 3e), which is very inactive for ion exchange.

Cesium Ion-Exchange Mechanism of Na-TSM and Release of Magnesium Ions. The higher ion-exchange selectivity for cesium ions than rubidium and potassium ions was revealed in Na-TSM through the K_d measurement mentioned above. Another important phenomenon was revealed based on a chemical analysis. Table 1 gives the amount of the sorbed alkali metal ions and the amount of sodium ions which were released from Na-TSM. Generally speaking, the ion-exchange of layered materials occurs between the metal ions in solution and the sodium ions which are located between each lamella of Na-TSM. If the assumption is really correct, the amount of sorbed ions must be equal to that of the released sodium ions. However, the amounts of sorbed alkali metal ions determined were much larger than the amounts of released sodium ions, except for the potassium ion-exchange at low concentration, as can be seen in Table 1. This result suggested that the ion-exchange on Na-TSM occurred not only with the sodium ions, but also with other ions from the octahedral layer of the Na-TSM lattice, e.g. magnesium ions. The presence of exchangeable magnesium ions has been proved to be due to an ion exchange with hydrogen ions in acidified clays.[12] A similar reaction has also been observed in the case of the water dispersion of Na-TSM even under neutral conditions.[13]

The release reaction of magnesium ions was actually observed, and the amounts of magnesium ions released into the supernatant solution after the ion-exchange reaction are listed in Table 2. If ion-exchange occurred among the three ions stoichiometry, assuming that the Na-TSM lattice did not collapse, the following equations should be valid:

$$\overline{Na^+} + M^+ \leftrightarrow Na^+ + \overline{M^+}, \quad (1)$$

$$\overline{Mg^{2+}} + 2M^+ \leftrightarrow Mg^{2+} + \overline{2M^+}, \quad (2)$$

$$A - (B + 2C) = 0, \quad (3)$$

Table 1. Amount of the Sorbed Alkali Metal Ions and Sodium Ions Released from Na-TSM

Concentration of metal ion/mol dm^{-3}		Amount of sorbed or released metal ion ($\times 10^{-4}$ mol/g TSM)		
		K^+	Rb^+	Cs^+
0.01	A	1.73	5.23	7.47
	B	0.95	1.10	1.35
0.003	A	0.62	1.93	3.00
	B	0.65	0.72	0.57
0.001	A	0.39	0.86	1.00
	B	0.48	0.43	0.48

A: amount of sorbed metal ions, B: amount of released sodium ions from Na-TSM. Volume of solution : 20 cm^3, Amount of Na-TSM : 0.2 g. 0.001 mol dm^{-3} corresponds to 1.00×10^{-4} mol g^{-1}.

Table 2. Amount of Released Magnesium Ion in Supernatant Solution after Ion Exchange

Concentration of metal ion/mol dm^{-3}	Amount of released magnesium ion ($\times 10^{-4}$ mol/g TSM)		
	K^+	Rb^+	Cs^+
0.01	0.97	2.49	3.32
0.003	0.57	0.98	1.45
0.001	0.79	0.45	0.37

Volume of solution : 20 cm^3, Amount of Na-TSM : 0.2 g. 0.001 mol dm^{-3} corresponds to 0.5×10^{-4} mol g^{-1}.

where A, B and C are the moles of sorbed alkali metal ions (M^+), released sodium ions (Na^+) and released magnesium ions (Mg^{2+}), respectively. The upper bar means the ions in the exchanger phase. Table 3 summarizes the results. The values of $A-(B+2C)$ were experimentally negative in all cases. This negative value must be ascribed to the collapse of the Na-TSM lattice. It is therefore clear that the Na-TSM used collapsed during the ion-exchange reaction with the amount of $A-(B+2C)$. Thus, the following equations can be applied to estimate the true amount of exchanged metal ions:

$$B' = B + \frac{A-(B+2C)}{6}, \tag{4}$$

$$C' = C + \frac{5\{A-(B+2C)\}}{6} \times \frac{1}{2}, \tag{5}$$

where B' and C' are the true amounts of exchanged sodium ions (Na^+) and magnesium ions (Mg^{2+}), respectively. The integer 6 is deduced from the chemical formula of Na-TSM,

Table 3. Stoichiometry of Ion Exchange Reaction of Na-TSM Involving Magnesium Ions

Concentration of metal ion/mol dm^{-3}		Amount of sorbed or released metal ion ($\times 10^{-4}$ mol/g TSM)		
		K^+	Rb^+	Cs^+
0.01	A	1.73	5.23	7.47
	B	0.95	1.10	1.35
	C	0.97	2.49	3.33
	A−(B+2C)	−1.16	−0.85	−0.54
	B′	0.757	0.958	1.26
	C′	0.487	2.136	3.105
0.003	A	0.62	1.93	3.00
	B	0.65	0.72	0.57
	C	0.58	0.98	1.45
	A−(B+2C)	−1.19	−0.75	−0.47
	B′	0.452	0.595	0.492
	C′	0.084	0.668	1.254
0.001	A	0.39	0.86	1.00
	B	0.48	0.43	0.48
	C	0.79	0.45	0.37
	A−(B+2C)	−1.67	−0.47	−0.22
	B′	0.202	0.352	0.443
	C′	0.094	0.254	0.278

A: amount of sorbed metal ions, B: total amount of released sodium ions from Na-TSM, C: total amount of released magnesium ions from Na-TSM, B′: amount of released sodium ions due to ion-exchange mechanism, C′: amount of released magnesium ions due to ion-exchange mechanism. Volume of solution : 20 cm^3. Amount of Na-TSM : 0.2 g. 0.001 mol dm^{-3} corresponds to 1.00×10^{-4} mol g^{-1}

Table 4. Separation Factors among K^+, Rb^+, Cs^+ and Na^+

	Na^+ < K^+	K^+ < Rb^+	Rb^+ < Cs^+
Zirconium phosphate[8]	3.4	2.8	2.3
Organic ion exchange resin[a)]	2.1	1.3	1.2
Na-taeniolite	131.1	1.1	1.3
Na-TSM	20.9	5.2	2.7

a) Amberlite® IR-120. Concentration of metal ion ($mol\,dm^{-3}$) : 0.01 (Na-TSM), 0.02 (Na-taeniolite).

$Na[Mg_{2.5}Si_4O_{10}F_2]\cdot 2H_2O$, i.e. $1(Na^+)+2\times 2.5(Mg^{2+})$; 1/2 in Eq. 5 means the valence of the magnesium ion. The calculated results are also shown in Table 3. Substituting B' and C' for B and C in Eq. 3, the stoichiometry can be applied to the ion-exchange mechanism of all of the alkali metal ions examined. These results suggest the possibility of a stoichiometric ion-exchange between the aqueous cesium ions and the lattice magnesium ions, as shown in Eq. 2. A slight amount of the magnesium ion-exchange was also observed in the case of rubidium ions. It is not yet clear whether the cesium ions possess the site of the inner lattice of Na-TSM or the interlayer of the lamellae within the limit of the present study. For further information, a detailed X-ray diffraction analysis should be required. The stoichiometry of the ion-exchange reaction on Li-hectorite could not be elucidated because the collapsed amount of Li-hectorite was too large and the reproducibility of the data was rather poor. In the case of Na-taeniolite, ion-exchange with magnesium ions was hardly observed within the limit of the experimental error.

The separation factor (α) of an ion-exchanger for the two species, A and B, is defined as

$$\alpha = \frac{K_{dA}}{K_{dB}},$$

where K_{dB} and K_{dA} are the distribution coefficients for the more strongly held species (B) and the less strongly held species (A), respectively. Based on this definition, α is always greater than unity. The separation factors of zirconium phosphate, an organic ion-exchange resin, Na-taeniolite and Na-TSM among sodium, potassium, rubidium and cesium ions are listed in Table 4. The larger the difference among the potassium, rubidium and cesium ion's separation factors is, the higher the ion selectivity is from the point of ion-exchange selectivity. Therefore, the selectivity difference of Na-TSM for cesium ions is the highest in all ion exchangers listed in Table 4. Na-taeniolite has the highest selectivity if only the separation factor between cesium ions and sodium ions is taken into consideration. In addition to the high selectivity difference of Na-TSM for cesium ions, a reverse ion-exchange reaction hardly occurred. Accordingly, Na-TSM must have a high potentiality as underground barriers to limit the spread of ^{137}Cs from the stratum disposal sites because of its high selectivity for cesium ions.

Conclusion

Sodium-type tetrafluorosilicic mica, Na-TSM, had the highest ion-exchange selectivity difference among cesium, rubidium and potassium ions. Once cesium ions were ion-exchanged in Na-TSM, they were hardly released due to the reverse ion-exchange with sodium ions. Such a property suggested that Na-TSM is a promising ion-exchange material for the fixation and stratum disposal of ^{137}Cs. The ion-exchange stoichiometry between (Cs^+, Rb^+, K^+) and (Na^++Mg^{2+}) was established if the collapse of Na-TSM lattice was taken into consideration. The stoichiometry indicated the cesium ion-exchange occurred with the lattice magnesium ions in addition to the interlayer sodium ions, although it was not clear whether the sorbed cesium ions were located inside the lattice layer or the interlayer space. If the former is true, ion exchange with the lattice magnesium ions as well as dehydration, which results in a shrinkage of the gallery height, must be an origin of such a strong fixation of cesium ions in Na-TSM.

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