Preparation of hydrated rubidium molybdenum bronze from hydrated sodium molybdenum bronze by ion exchange, and its characterization and thermal decomposition[†]

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A new type of hydrated rubidium molybdenum bronze has been synthesized, which was very unstable. It gave a orthorhombic structure with lattice constants $a=3.74(1)$, $b=22.82(7)$, and $c=3.85(1)$ Å. Exchange of Na^+ ion with Rb^+ ion took place within 30 s. The exchange reaction, $[Na^+(H_2O)_n]_x[MoO_3{}^{x-}]+Rb^+ \leftrightarrows [Rb^+(H_2O)_n]_x[MoO_3{}^{x-}]+Na^+$, took place in both directions by changing the Na^+/Rb^+ ratio in the mixed solution. A concentration of about 0.05 mol Na in the sample was the minimum value necessary to retain the structure of hydrated sodium molybdenum bronze. We obtained the blue rubidium bronze, $Rb_{0.30}MoO_3$, by heating hydrated rubidium bronze in nitrogen. This is a new route to producing the metal bronze at low temperature. We also obtained rubidium decamolybdate by heating it in air. This is also a new method for producing rubidium decamolybdate by solid-state reaction.

It is well known that MoO_3 has a layer structure which consists of two-dimensional sheets built up with MoO_6 octahedra. The sheets are separated by a van der Waals gap, and guest cations are inserted between the sheets. When MoO_3 is suspended in a neutral aqueous electrolyte solution in the presence of a strong reducing reagent, the hydrated alkali molybdenum oxide bronzes, $[A^+(H_2O)_n]_x[MoO_3]^{x-}$, are prepared according to eqn. (1)

$$xA^+ + xe^- + nxH_2O + MoO_3 \rightarrow [A^+(H_2O)_n]_x[MoO_3]^{x-} \qquad (1)$$

The hydrated alkali molybdenum bronzes have been obtained by Schöllhorn *et al.*,[1] Son *et al.*,[2] Iwamoto *et al.*,[3] and Thomas and McCarron.[4] The MoO_3 layers take up an electron from the reductant molecules and are negatively charged. An equivalent amount of hydrated cations from electrolyte solution is entered simultaneously into the interlayer space. There is no suitable reducing reagent for MoO_3 except sodium dithionate ($Na_2S_2O_4$). Recently, Zhu and Manthiram[5] obtained Na_xWO_3, K_xMoO_3 and $K_{0.85}Mo_6O_{17}$ by using alkali-metal borohydrides such as $NaBH_4$ and KBH_4 as effective reducing reagents in aqueous solution; however, they could not produce hydrated alkali-metal bronzes. $Na_2S_2O_4$ can easily give the hydrated sodium bronzes according to eqn. (2).

$$x/2Na_2S_2O_4 + MoO_3 + nxH_2O \rightarrow [Na^+(H_2O)_n]_x[MoO_3]^{x-} + xSO_2 \qquad (2)$$

An ideal composition of hydrated sodium bronze is $[Na^+(H_2O)_n]_{0.25}[MoO_3]^{0.25-}$ $(n \geqslant 1)$.[6] However, a partial replacement of Na^+ ions by protons takes place[1,6] and partially inserted protons occupy the same intra-proton sites which protons in the type I hydrogen bronze occupy. Other hydrated alkali-metal bronzes can be obtained by cation exchange from $[Na^+(H_2O)_n]_x[MoO_3]^{x-}$ according to eqn. (3).

$$[Na^+(H_2O)_n]_x[MoO_3]^{x-} + xA^+ \rightarrow [A^+(H_2O)_n]_x[MoO_3]^{x-} + xNa^+ \quad (A = Li, K, Rb, Cs) \qquad (3)$$

There have been no precise studies on the mechanism of ion exchange of Na^+ ions with other alkali-metal ions, A^+. In this work, we tried to obtain the hydrated rubidium bronze from hydrated sodium bronze by ion exchange reaction according to eqn. (4).

$$[Na^+(H_2O)_n]_x[MoO_3]^{x-} + xRb^+ \rightarrow [Rb^+(H_2O)_n]_x[MoO_3]^{x-} + xNa^+ \qquad (4)$$

We obtained and characterized two types of hydrated rubidium bronzes: one is a stable hydrated bronze as reported by Schöllhorn *et al.*[1] and Thomas and McCarron;[4] the other is a new type of hydrated rubidium bronze which has not previously been reported. We also tried to determine the mechanism and driving force for ion exchange. At the same time, we attempted to carry out the reverse exchange reaction according to eqn. (5).

$$[Rb^+(H_2O)_n]_x[MoO_3]^{x-} + xNa^+ \rightarrow [Na^+(H_2O)_n]_x[MoO_3]^{x-} + xRb^+ \qquad (5)$$

We found interesting results for cation exchange and reverse exchange, and will discuss the cation exchange reaction in detail.

On the other hand, as has been reported previously, when the hydrated sodium and potassium bronzes were heated in nitrogen the purple sodium bronze,[7] $Na_{0.88}Mo_6O_{17}$, and the blue potassium bronze,[8] $K_{0.30}MoO_3$, were obtained at about 600 K. This temperature is lower by about 200 K than that of the usual fused method. This method is a new route to production of the metal bronze. When they are heated in air, they are decomposed to $Na_2Mo_4O_{13}$ [9] and K_2MoO_4,[10] respectively. In the case of the hydrated rubidium bronzes, by heating them in nitrogen and in air we obtained blue rubidium bronze, $Rb_{0.30}MoO_3$ and rubidium decamolybdate, respectively. These results will be also discussed.

Experimental

Sample preparation

The hydrated sodium bronze (HyNa) was prepared by the method of Schöllhorn *et al.*[1] and Thomas and McCarron.[4] It was dried in air (AD) or under vacuum. The composition was $[Na(H_2O)_n]_{0.22\text{–}0.23}MoO_3$, where $n \geqslant 1$. The hydrated rubidium bronze (HyRb) was prepared by cation exchange.

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HyNa(AD) was suspended in 1 mol aqueous RbCl solution at room temperature for 1 day. During the reaction nitrogen gas was bubbled into the solution to prevent oxidation of the product. It was collected by suction filtration and was washed with distilled water until the filtrate was colorless. The product after filtration was named HyRb(AD). This was unstable and changed quickly to another phase with the composition $[Rb(H_2O)_n]_{0.22-0.23}MoO_3$, where $n \geqslant 2$. The product dried under vacuum (VD) or left in air for more than 2 days was stable and gave a single phase, HyRb(VD), with composition $[Rb(H_2O)_n]_{0.22-0.23}MoO_3$ ($n = 0.7$–1.2).

Characterization

All powder X-ray diffraction (XRD) patterns were obtained using a Rigaku RINT 1200M diffractometer and reflections were measured using Cu-Kα_1 ($\lambda = 1.54056$ Å) radiation. TG–DTA curves were obtained using a Mac Science TG–DTA 2000 instrument with a heating rate of 10 K $\min^{-1}$.

The Na, Rb, and Mo contents in the samples were measured using a Hitachi atomic absorption spectrometer with the 330.23 nm line for Na, the 780.02 nm line for Rb, and the 313.26 nm line for Mo. Mo^{5+} was determined by the method of Choain and Marion.[11]

Results and Discussion

Preparation of hydrated rubidium bronze (HyRb)

HyNa(AD) was suspended in 1 mol aqueous RbCl solution at 298 K. According to chemical analysis, the exchange of Na^+ ion with Rb^+ ion took place within 30 s. Fig. 1 shows the XRD patterns of the exchanged samples. The sample immediately after filtration gives an XRD pattern as shown in Fig. 1(C), which is a mixture of at least two phases. To prevent oxidation, the sample after filtration was covered with a polyvinylidene chloride film and the XRD pattern was obtained as shown in Fig. 1(B). The pattern included those peaks due to polyvinylidene chloride. Fig. 1(A) is the pattern due to HyNa(AD) and the main peaks are very similar to those of Fig. 1(B). The stable XRD pattern due to the sample dried under the vacuum for over night was obtained as shown in Fig. 1(D), which is identical with the XRD pattern due to the sample left for two days in air at room temperature. This is very stable and, therefore, the pattern should be due to a single phase, HyRb(VD). From the X-ray results of Fig. 1(D), we could calculate the *d* values and indexings of HyRb(VD) as shown in Table 1. The lattice constants were also estimated. The peaks due to HyRb(VD) were cancelled from those due to the wet sample (C). The remaining peaks agreed well with those of the sample with a polyvinylidene film, except for the peaks due to the film and a few other peaks. By using these results, we calculated the *d* values and compared them with those of observed ones; these were found to be identical. Therefore, these patterns should be due to the single phase, HyRb(AD). The lattice constants and indexings are summarized in Table 2. The observed d_{020} values of HyRb(AD) and HyRb(VD) are 11.413 and 9.461 Å, respectively. Schöllhorn *et al.*[1] and Thomas and McCarron[4] reported d_{020} values for the hydrated rubidium bronze of 9.51 and 9.49 Å, respectively, which are in good agreement with 9.461 Å; however HyRb(AD) with d_{020} of 11.413 Å has not been reported. Therefore, this

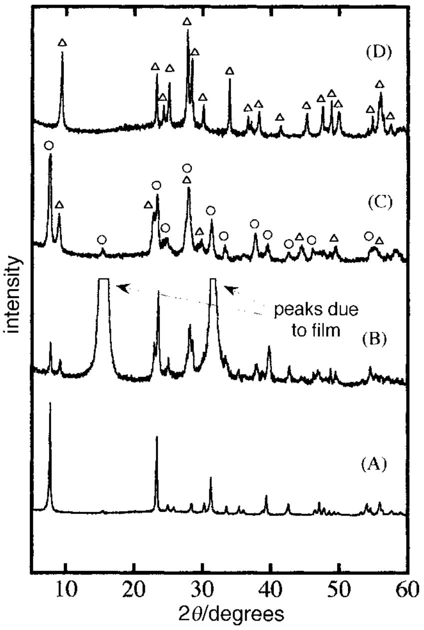

Fig. 1 XRD patterns of the samples: (A) hydrated sodium bronze, HyNa(AD), (B) hydrated rubidium bronze covered with a polyvinylidene chloride film after filtration, HyRb (covered with polyvinylidene chloride), (C) hydrated rubidium bronze after filtration, HyRb (wet), and (D) vacuum-dried hydrated rubidium bronze, HyRb(VD). ○, HyRb(AD); △, HyRb(VD).

Table 1 Indexing of HyRb(VD)[a]

$2\theta/°$	*h*	*k*	*l*	*d*(calc)/Å	*d*(obs)/Å
9.31	0	2	0	9.488	9.461
18.69	0	4	0	4.744	4.761
23.26	0	0	1	3.821	3.824
24.32	1	1	0	3.657	3.657
25.10	0	2	1	3.545	3.542
27.76	1	3	0	3.211	3.206
28.19	0	6	0	3.163	3.137
30.00	0	4	1	2.976	2.965
33.90	1	1	1	2.642	2.641
36.52	1	3	1	2.458	2.455
36.86	0	6	1	2.436	2.426
37.90	0	8	0	2.372	2.354
41.33	1	5	1	2.182	2.186
45.28	1	8	0	2.001	2.003
47.55	0	0	2	1.911	1.910
48.83	2	0	0	1.864	1.863
49.82	2	2	0	1.829	1.827
54.11	1	1	2	1.694	1.693
54.20	1	10	0	1.691	1.691
54.76	2	0	1	1.675	1.674
54.81	1	2	2	1.674	1.673
55.68	2	2	1	1.650	1.648
56.20	0	6	2	1.635	1.633

[a] Crystal system: orthorhombic; lattice constants: $a = 3.727(1)$, $b = 18.98(3)$, $c = 3.821(6)$ Å.

Table 2 Indexing of HyRb(AD)[a]

$2\theta/°$	*h*	*k*	*l*	*d*(calc)/Å	*d*(obs)/Å
7.74	0	2	0	11.412	11.413
15.52	0	4	0	5.706	5.701
23.36	0	6	0	3.804	3.802
23.39	0	1	1	3.799	3.783
25.03	1	2	0	3.555	3.559
27.92	0	4	1	3.193	3.164
28.51	1	4	0	3.129	3.127
30.33	0	5	1	2.944	2.990
31.33	0	8	0	2.853	2.855
33.36	1	0	1	2.684	2.690
38.89	1	5	1	2.314	2.327
39.45	0	10	0	2.282	2.290
39.70	1	8	0	2.269	2.267
42.64	0	9	1	2.118	2.114
47.31	0	1	2	1.919	1.916
53.45	1	0	2	1.713	1.713
54.49	2	0	1	1.683	1.681

[a] Crystal system: orthorhombic; lattice constants: $a = 3.74(1)$, $b = 22.82(7)$, $c = 3.85(1)$ Å.

leads to the conclusion that this HyRb(AD) with d_{020} of 11.413 Å is a new phase of the hydrated rubidium bronze. The composition of HyRb(AD) is $[Rb(H_2O)_n]_{0.22-0.23}MoO_3$ ($n \geq 2$) and that of HyRb(VD) is $[Rb(H_2O)_n]_{0.22-0.23}MoO_3$ ($n=$ 0.7–1.2), according to TG and chemical analyses.

HyRb(VD) showed IR bands at 955 and 581 cm^{-1} and HyNa(VD) showed bands at 956 and 586 cm^{-1}; both bands are very similar. In the case of MoO_3 the band assigned to Mo=O double bonds appeared at 997 cm^{-1}.[12] The band at 955 cm^{-1} is due to Mo=O double bonds, which are weakened by insertion of Rb^+ ions, as in the case of Na^+ ion insertion.[6] However, there is no large difference in the effect between Na^+ ion and Rb^+ ion.

HyRb(VD) was observed by proton NMR spectroscopy at room temperature and at 77 K. The spectrum at room temperature is narrowed by a motion, which shows the movement or rotation of H_2O molecules in the bronze. This is very similar to that of HyNa(VD).[6] The spectrum at 77 K is considered to be a superposition of at least two components, a narrow line and a broader one with side peaks. The broader line is similar to a Pake doublet, which is attributed to a proton pair[13] due to the hydrate water. The narrow central peak is due to a Gaussian-like line arising from isolated protons in fixed positions.

Cation exchange reaction

HyNa(VD) was suspended in an aqueous solution of which the total concentration of Rb+Na was 1 mol. The concentration of Rb^+ ion in solution changed from zero to 100%. Fig. 2 shows the change in d_{020} of the sample obtained by changing the Rb/Na ratio in the mixed solution. Curve (1) gives the exchange of Na^+ ion with Rb^+ ion. The d value is nearly constant at about 9.54 Å till 50% Rb^+ ion in the solution, but at >50% it decreases to about 9.45 Å and then is constant. The sample with $d=9.54$ Å is due to HyNa(VD) and the other with $d=9.45$ Å to HyRb(VD). This indicates that the HyNa(VD) structure was changed to the HyRb(VD) structure at 50% Rb^+ ion content. On the other hand, curve (2) gives the reverse exchange from Rb^+ ion to Na^+ ion. The d value of 9.45 Å is constant till 50% Na^+ ion, but it increases to $d=9.54$ Å beyond 50% Na^+. This means that the HyRb(VD) structure changed to the HyNa(VD) structure.

Fig. 3 shows the change in the content of A (A = Na, Rb) in the bronze obtained by cation exchange in mixed aqueous solutions with various Na/Rb ratios. Curve (1) shows the exchange of Na^+ ion with Rb^+ ion and curve (2) the reverse exchange. In the case of exchange of Na^+ ion with Rb^+ ion, Na^+ ion is completely replaced by Rb^+ ion, but in the case of reverse reaction, Rb^+ ion is not completely replaced by Na^+ ions. It is clear that the exchange of Na^+ ion with Rb^+ ion is easier than that of Rb^+ ion with Na^+ ion. In both exchange reactions, the d value changes at 50% of Rb^+ ion in the solution and the contents of Na^+ ion in the exchanged samples always fall in the range 0.02–0.06 mol, which corresponds to about 1/5 of the ideal value of 0.25 mol. This is the minimum value needed to retain the HyNa(VD) structure. That is, the HyNa(VD) structure begins to change to the HyRb(VD) structure when the Na/Mo ratio is about 0.05. It is necessary that the exchange of Rb^+ ion with Na^+ ion should expand the interlayer space. Considering these results, there is a difference in cation exchange between Na^+ ion with Rb^+ ion and Rb^+ ion with Na^+ ion.

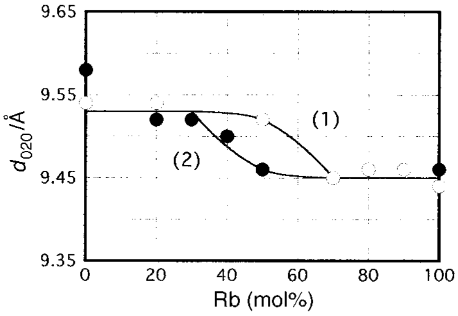

Fig. 2 Change in d_{020} of exchanged samples. (1) Exchange from HyNa(VD) to HyRb(VD), (2) from HyRb(VD) to HyNa(VD).

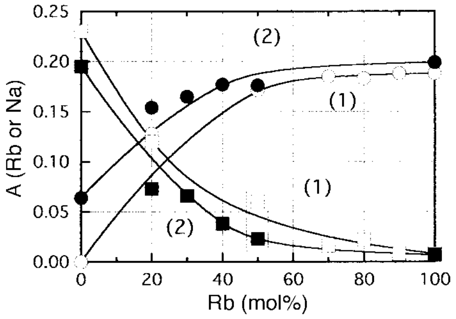

Fig. 3 Change in the contents of Rb and Na in the exchanged samples. (1) Exchange from HyNa(VD) to HyRb(VD) (○, Rb; □, Na), (2) from HyRb(VD) to HyNa(VD) (●, Rb; ■, Na).

Fig. 4 shows the change in d_{020} and the Rb^+ and Na^+ ion contents in the exchanged samples when HyNa(VD) was suspended in RbCl aqueous solutions of various concentrations. The d_{020} value began to decrease at 40% Rb^+ ion and reached a constant value at 50%. The interlayer spacing began to decrease at Na/Mo≈0.06, which corresponds to the same value as in the case of the mixed solution. According to Fig. 4, it is clear that Na^+ ion in the sample is rapidly removed and the content of Rb^+ ion increases rather linearly. The d value decreases sharply at 0.06 mol Na. The behavior of Rb^+ ion is a little different from that of Na^+ ion. Considering the above results, Na^+ ion in the sample plays an important role in the exchange. That is, in order that the HyNa(VD) structure is retained, Na/Mo ratio in the bronze must be about 0.05 which corresponds to 1/5 of the ideal composition.

Fig. 5 shows the total Na and Rb contents in the exchanged bronzes. The x value (Mo^{5+}/Mo) of the bronze is also shown in Fig. 5; it is constant. The amount of Na+Rb gradually decreases in the range between 0 and 50% Rb^+ ion in the mixed solution and remains constant in the range between 50 and 100%. There is a difference between the x value and the

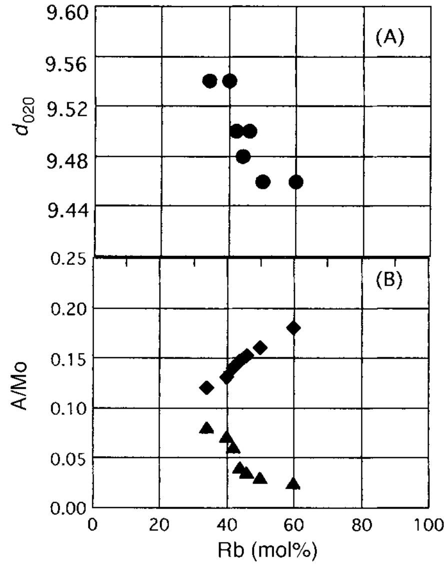

Fig. 4 Changes in (A) d_{020} value (●) and in (B) the Rb (◆) and Na (▲) contents in the samples exchanged in various concentrations of RbCl solution

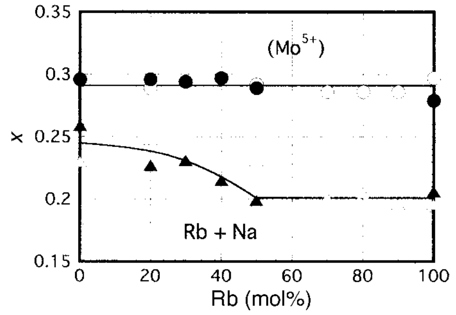

Fig. 5 Change in the contents of Rb+Na (△ and ▲) and in the x value (○ and ●) in the samples exchanged in the mixed solution. ○ and △, from HyNa(VD) to HyRb(VD); ● and ▲, from HyRb(VD) to HyNa(VD).

total amount of Na+Rb, which corresponds to the amount of inserted protons. Indeed, the NMR results prove the existence of the protons. In the case of HyNa(VD), it has been reported that 0.02–0.03 mol of protons were included. The proton content is smaller when the Na^+ content in the sample is larger. In the range >50% Rb^+ ion, the proton content is large and remains constant. Considering chemical, NMR and X-ray results, it is assumed that the insertion of protons has an effect on the insertion of cations. Miyazaki[14] reported that protons in the bronze affected the insertion of cations; the following reasons for this are possible: an Na^+ ion site in the interlayer of MoO_3 is different from that of an Rb^+ ion, and there are differences in the interaction between protons and inserted cations.

The Δd is obtained from the d_{020} value of the hydrated alkali bronze by subtracting the d_{020} value of MoO_3. It is a measure of the expansion when the hydrated alkali-metal ions are inserted into an interlayer of the host material. The Δd of the alkali hydrated bronzes (VD) is plotted against ionic radius[15] in Fig. 6. This clearly shows the presence of two types of hydrated bronzes (VD). One is a group of Li, Na, and K, and the other that of K, Rb, and Cs. It is reported there are two types of HyK(VD).[10] The ionic radius of the former group is smaller than that of the latter, which indicates the difference in the manner of insertion. The fact that the Δd of hydrated bronzes with larger ionic radii is rather smaller means that cations are closely packed in the interlayer. It is suggested that the cations are located in the body center of the terminal oxygens of MoO_6 octahedra. Thomas and McCarron[4] proposed two types of hydrated alkali bronzes. One is a six-coordinate type, *i.e.* the alkali ion is located at the face center of four terminal oxygens of MoO_6 octahedra and each oxygen of H_2O is associated with both sides of the alkali ion as shown in Fig. 7. Sotani *et al.*[6] proposed a model of hydrated Na^+ ion insertion in HyNa(VD), which agreed well with the six-coordinate model. The second type is an eight-coordination type, in which the alkali ion is located at the body center of eight terminal oxygens. Rb^+ ion in HyRb(VD) has a different site from Na^+ ion in HyNa(VD).

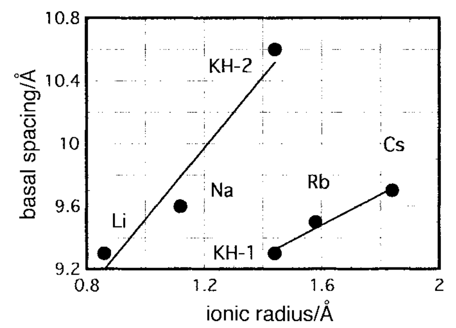

Fig. 6 Relation between an ionic radius and Δd of hydrated alkali bronzes. $\Delta d = d_{020}$ (hydrated alkali bronze) $- d_{020}$ (MoO_3).

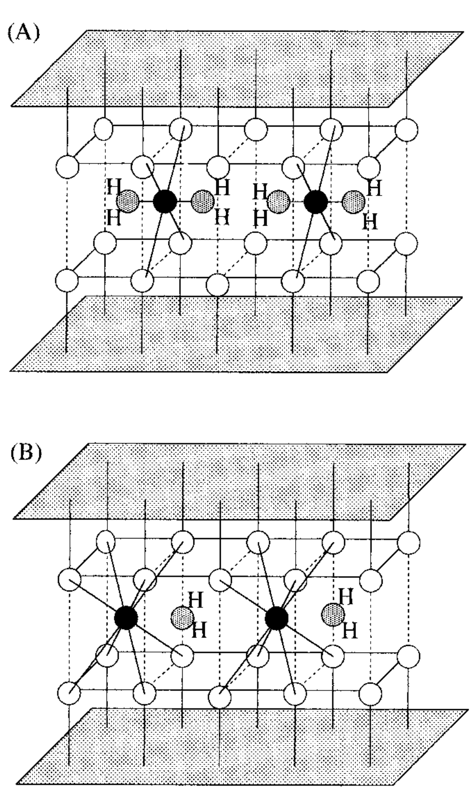

Fig. 7 Models of hydrated alkali metal bronzes: (A) 6-coordination, (B) 8-coordination

$$[Na^+(H_2O)_n]_x[MoO_3]^{x-} + xRb^+ \leftrightarrows [Rb^+(H_2O)_n]_x[MoO_3]^{x-} + xNa^+ \qquad (6)$$

Eqn. (6) takes place reversibly by changing the concentration of cations in the aqueous solution. This suggests that the concentration of ions in the solution plays a very important role in the cation exchange. However, Rb^+ ion is easier to exchange with Na^+ ion, although its ionic radius is larger. Moreover, Rb^+ ion can be easily introduced when the Na content in the sample is about 0.05 mol. Na^+ ions in the sample are completely replaced with Rb^+ ions, but Rb^+ ions are not replaced completely.

What is the difference in the behavior between Na^+ ions and Rb^+ ions? One difference is the condensive difference in the site of the hydrated cation: HyNa(VD) is the six-coordinate and HyRb(VD) is eight-coordinate. Which type the cation can select depends on the difference in the ionic radii and the strength of the interaction between the hydrated cation and the terminal oxygen of MoO_6 octahedra. The hydration energies of Na^+ and Rb^+ ions are 406 and 293 kJ mol^{-1}, respectively.[15] This suggests that the strength of interaction of Na^+ ions is stronger than that of Rb^+ ions. Na^+ ion can adopt a stable position by interaction with four terminal oxygens of MoO_6 octahedra as shown in Fig. 7(A). Therefore, though the ionic radius of Na^+ ion is smaller, Δd is larger. On the other hand, an Rb^+ ion located at the center of eight terminal oxygens of an MoO_6 octahedron is stable and is closely packed as shown in Fig. 7(B). Therefore, Rb^+ ion is not replaced completely by Na^+ ion. This may depend on geometrical reasons.

Heat treatment in nitrogen and in air

In nitrogen. Fig. 8(A) shows TG–DTA curves of HyRb(VD) treated in nitrogen. The endothermic peaks appeared at around 343 and 463 K, which accompanied mass losses, and at 856

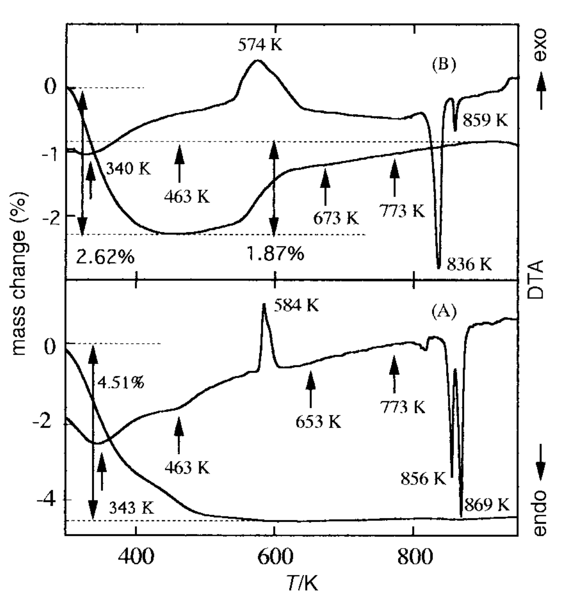

Fig. 8 TG–DTA curves of HyRb(VD) in nitrogen (A) and in air (B)

and 869 K, which accompanied no mass losses. The former may correspond to dehydration and the latter to melting. An exothermic peak appeared at 584 K, which did not appear upon cooling, which indicates that it should be an irreversible process. The sample was heated in nitrogen at the temperatures marked by arrows in Fig. 8(A). Table 3 shows the results of chemical analysis. According to these results, it is clear that Rb/Mo and x (Mo^{5+}/Mo) remain constant for all samples heated at various temperatures. Though HyRb(VD) changed irreversibly, this means that the samples keep the mixed valence state of Mo.

Fig. 9 shows XRD patterns of HyRb(VD) heated in nitrogen at the temperatures marked by arrows in the TG–DTA curve. The samples heated to 463 K show peaks due to the vacuum-dried structure. The sample heated at 653 K, which is just after the exothermic peak, shows new XRD peaks due to $Rb_{0.30}MoO_3$ and MoO_3. These XRD patterns are also found for the sample heated at 973 K, even though it passes through the melting temperature. The blue rubidium bronze, $Rb_{0.30}MoO_3$, is produced as in the case of the blue potassium bronze, $K_{0.30}MoO_3$,[10] according to eqn. (7). This is also a new route to the production of $Rb_{0.30}MoO_3$ at low temperatures.

$$\begin{array}{ll} Rb_{0.23}MoO_3\cdot 0.22H_2O \xrightarrow{H_2O\uparrow} & \\ Rb_{0.23}MoO_3 \xrightarrow{584\ K} Rb_{0.30}MoO_3 + MoO_3 & \\ \text{isomorphous with vacuum-dried structure} & (7) \end{array}$$

The samples which were obtained by exchange reaction in mixed solutions of various Rb/Na ratios were heated in nitrogen. XRD patterns of the heated samples consist of $Rb_{0.30}MoO_3$, $Na_{0.88}Mo_6O_{17}$ and MoO_3. The relative intensities of the main XRD peaks due to $Rb_{0.30}MoO_3$ and $Na_{0.88}Mo_6O_{17}$ are very similar to the results of chemical analyses. This suggests that we can control the desired cation:cation ratio and obtain the desired mixed-metal bronze by cation exchange.

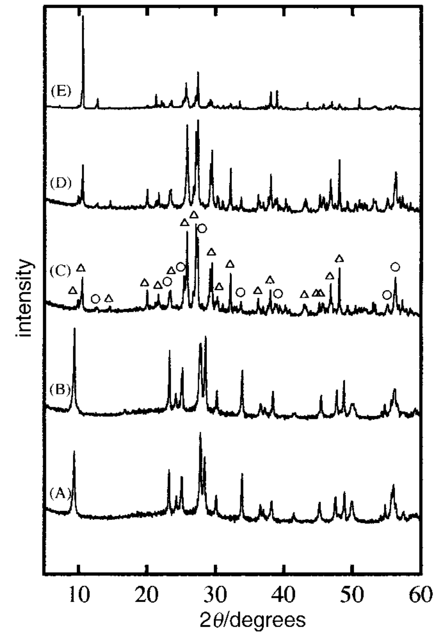

Fig. 9 XRD patterns of HyRb(VD) heated in nitrogen. (A) HyRb(VD), treated at (B) 463 K, (C) 653 K, (D) 773 K, and (E) 973 K. △, $Rb_{0.3}MoO_3$; ○, MoO_3.

In air. HyRb(VD) was heated in air; Fig. 8(B) shows the TG–DTA curves. An endothermic peak with loss of mass appeared at about 340 K, and those with no mass loss at 836 and 859 K. The former is due to dehydration and the latter to melting. An exothermic peak with mass gain appeared at 574 K, but upon cooling no DTA peak appeared. This suggests that this change is the irreversible process. HyRb(VD) heated at temperatures marked by arrows were analyzed chemically; the results are shown in Table 4. The Rb/Mo ratio was kept constant, but the x (Mo^{5+}/Mo) value decreased to zero at 673 K. This means that Mo^{5+} is completely oxidized to Mo^{6+}. Fig. 10 shows XRD patterns of the sample used in the chemical analysis. HyRb(VD) heated above 673 K shows peaks due to a mixture of MoO_3 and rubidium decamolybdate. As mentioned above, the TG curve shows a mass gain, which indicates the oxidation of samples. Indeed, according to chemical analysis, Mo^{5+} is completely oxidized to Mo^{6+} at 673 K. Moreover, according to the NMR results, HyRb(VD) contains a small number of protons. In the case of hydrogen bronze, protons reacted with the lattice oxygens and were released as H_2O.[16] Therefore, the protons in HyRb(VD) reacted with lattice oxygens and the vacant sites of lattice oxygens were oxidized at 673 K accompanied by a mass gain. Considering the above results, it is clear that HyRb(VD) is oxidized completely, and is changed to MoO_3 and rubidium decamolybdate, according

Table 3 Results of chemical analysis of HyRb(VD) heated in nitrogen

treatment temp./K	Rb/Mo	H_2O/Mo	H_2O/Rb	x (Mo^{5+}/Mo)	composition
—[a]	0.22	0.44	2.0	0.22	$Rb_{0.22}MoO_3\cdot 0.44H_2O$
343	0.23	0.22	1.0	0.23	$Rb_{0.23}MoO_3\cdot 0.22H_2O$
463	0.23	0	0	0.22	$Rb_{0.23}MoO_3$
653	0.23	0	0	0.20	$Rb_{0.23}MoO_3$
773	0.22	0	0	0.21	$Rb_{0.22}MoO_3$

[a] Vacuum-dried sample.

Table 4 Results of chemical analysis of HyRb(VD) heated in air

treatment temp./K	Rb/Mo	H_2O/Mo	H_2O/Rb	x (Mo^{5+}/Mo)	composition
—[a]	0.22	0.44	2.0	0.22	$Rb_{0.22}MoO_3 \cdot 0.44H_2O$
343	0.22	0.22	—	0.15	$Rb_{0.22}MoO_3 \cdot nH_2O$
463	0.23	0	0	0.02	$Rb_{0.23}MoO_3$
673	0.23	0	0	0	$Rb_{0.23}MoO_3$
773	0.23	0	0	0	$Rb_{0.23}MoO_3$

[a] Vacuum-dried sample.

to eqn. (8). It is difficult to synthesize rubidium decamolybdate. This is a new method to obtain rubidium decamolybdate containing MoO_3 as an impurity.

$$Rb_{0.22}MoO_3 \cdot 0.22H_2O \xrightarrow{H_2O\uparrow}$$

$$\underset{\substack{\text{isomorphous with}\\ \text{vacuum-dried}\\ \text{structure}}}{Rb_{0.23}MoO_3} \xrightarrow{O_2\downarrow} MoO_3 + \text{Rb decamolybdate} \qquad (8)$$

Conclusions

(1) The exchange reaction of Na^+ ions with Rb^+ ions takes place completely within 30 s. (2) HyRb(AD) is a new hydrated rubidium bronze with orthorhombic structure with lattice constants of $a = 3.74(1)$, $b = 22.82(7)$ and $c = 3.86(1)$ Å. (3) When the concentration of Na^+ or Rb^+ ions in the mixed solution is $>50\%$, a change from the HyNa(VD) structure to the HyRb(VD) structure or from the HyRb(VD) structure to the HyNa(VD) structure proceeds. Structural changes from HyNa(VD) to HyRb(VD) begin to take place when the content of Na in the sample is close to about 0.05 mol. Na^+ ion is completely replaced by Rb^+ ion, but Rb^+ ion can not be completely replaced by Na^+ ion. (4) The insertion site of Na^+ ions is different from that of Rb^+ ions. Na^+ ions occupy six-coordinate sites and Rb^+ ions eight-coordinate sites. The driving force for the exchange reaction and the reverse reaction depends on (i) the concentration of ions in the mixed solution and (ii) the insertion site of ions in the interlayer space, which result from the difference in the strength of interaction. (5) HyRb(VD) was changed to a mixture of $Rb_{0.30}MoO_3$ and MoO_3 by heating in nitrogen and decomposed to a mixture of rubidium decamolybdate and MoO_3 upon heating in air.

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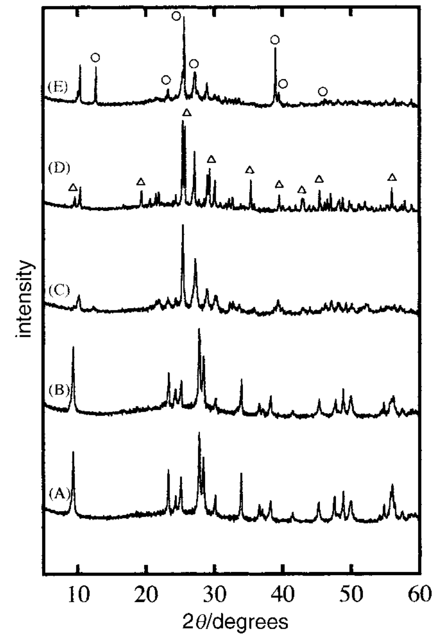

Fig. 10 XRD patterns of the samples heated in air. (A) HyRb(VD), heated at (B) 463 K, (C) 673 K, (D) 773 K, and (E) 973 K. △, rubidium decamolybdate; ○, MoO_3.

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