

Preparation of Hydrated Potassium Molybdenum Bronzes and Their Thermal Decomposition

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Three kinds of hydrated potassium bronze, $K_{0.23}(H_2O)_{0.65}MoO_{3.00}$ (HyK-AD), $K_{0.23}(H_2O)_{0.43}MoO_{3.00}$ (HyK-H2), and $K_{0.23}(H_2O)_{0.27}MoO_{3.00}$ (HyK-H1), were obtained from hydrated sodium bronzes by cation exchange. Hydrated potassium bronzes dried under vacuum are of two types. The first, HyK-H2, belongs to the six-coordination type and the second, HyK-H1, belongs to the eight-coordination type. When hydrated bronzes were heated in nitrogen, they turned into a mixture of the blue potassium bronze, $K_{0.3}MoO_3$, and MoO_3 . In contrast, those heated in air decomposed to $K_2Mo_4O_{13}$ and MoO_3 . © 1997

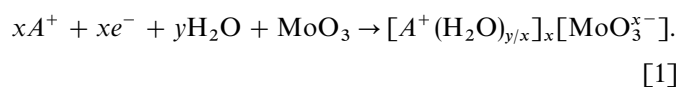
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INTRODUCTION

Alkali metal molybdenum bronzes have been of interest due to their interesting physical properties. They have potential for such technological applications as battery electrodes and electrochromic devices. The first alkali molybdenum oxide bronzes were prepared by Wold *et al.* (1). Ramanujachary *et al.* (2) obtained a single crystal of alkali metal molybdenum bronzes by temperature gradient flux technique. This method requires a high temperature of more than 800 K to melt starting materials. Manthiram *et al.* (3) heated the products of the reduction of aqueous A_2MoO_4 with ABH_4 (A = alkali metal) and obtained alkali metal bronzes at 623 ~ 773 K. This is a new route to obtain

bronzes at lower temperatures. The authors obtained the purple sodium bronze, $Na_{0.9}Mo_6O_{17}$ (4), and the blue potassium bronze, $K_{0.3}MoO_3$ (5), by heating each hydrated alkali molybdenum bronze in nitrogen at low temperature. This is a new and interesting preparation method to obtain alkali metal bronzes in which the synthesis temperature is lower than that of the usual melt methods by about 200 K and, moreover, the reaction proceeds in the solid state from hydrated alkali bronze to alkali metal bronze. However, this new method has a weak point in that the metal bronze produced contained a small amount of MoO_3 . To obtain the single phase of alkali metal bronzes from the hydrated bronze by heat treatment in nitrogen, it is necessary to control the amount of alkali metal ion in the hydrated bronzes (6). Therefore, it should be studied precisely on properties of the hydrated alkali bronzes.

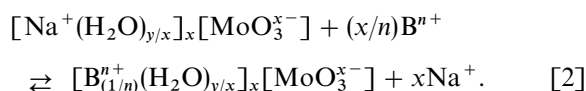
The hydrated alkali bronzes, $[A^+(H_2O)_{y/x}]_x[MoO_3^{x-}]$, are obtained according to



MoO_3 must be reduced before any of the guest cations are inserted. Sodium dithionate, $Na_2S_2O_4$, is a conventional reducing reagent for MoO_3 (7–10). The hydrated sodium bronzes, $[Na^+(H_2O)_{y/x}]_x[MoO_3^{x-}]$ are easily obtained using this reagent. The x value of the ideal composition of the hydrated sodium bronze is 0.25, but a partial replacement of Na^+ ions with protons usually takes place (11). There is no useful alkali reagent for reduction except sodium dithionate. Therefore, other bronzes can be obtained only by cation

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exchange in an ambient electrolyte solution according to



It is well known that most of this exchange takes place rapidly (7). However, there is no further precise information on the cation exchange. We reported (11) in detail on hydrated sodium bronzes and proposed the models of hydrated sodium bronzes. Also, there are only a few reports on other hydrated alkali bronzes (7–10), but not much information. Recently, Tsang *et al.* (12) obtained potassium metal bronzes such as $\text{K}_{0.26}\text{MoO}_3$, $\text{K}_{0.30}\text{MoO}_3$, and $\text{K}_{0.85}\text{Mo}_6\text{O}_{17}$ by heating the reduction products of aqueous K_2MoO_4 with aqueous KBH_4 . However, we first tried to synthesize the hydrated potassium bronzes by ion exchange and to characterize the exchanged hydrated potassium bronzes. We confirmed three types of hydrated potassium bronzes. By heating them in nitrogen they were changed to the blue potassium bronze, $\text{K}_{0.3}\text{MoO}_3$, and MoO_3 , and by heating in air they were changed to $\text{K}_2\text{Mo}_4\text{O}_{13}$ and MoO_3 . These will be reported in detail.

EXPERIMENTAL

Procedures of Ion Exchange

Hydrated potassium bronzes were prepared by the method of cation exchange (7, 10). An air-dried hydrated sodium bronze (HyNa–AD), $[\text{Na}(\text{H}_2\text{O})_{4.26}]_{0.23}\text{MoO}_3$, and a vacuum-dried hydrated sodium bronze (HyNa–VD), $[\text{Na}(\text{H}_2\text{O})_{1.95}]_{0.23}\text{MoO}_3$, were used as starting materials for the ion exchange. 0.5 g of HyNa–AD or HyNa–VD was suspended in 50 cm³ of 1 M aqueous KCl solution, which was stirred with a magnetic stirrer maintained at 300 ~ 304 K for the desired time. During the experiment, nitrogen gas was bubbled to prevent oxidation of the exchanged sample. The sample was collected by suction filtration and then washed with distilled water until Cl^- ions were not detected.

Measurements

Thermal gravimetric–differential thermal analysis (TG–DTA) studies were carried out both in air and in nitrogen using a Mac Science TG–DTA 2000 with a heating rate of 10 K min⁻¹. X-ray diffraction (XRD) patterns of the sample were obtained using a Rigaku RINT 1200M X-ray diffractometer with $\text{CuK}\alpha$ radiation. The XRD patterns at high temperatures were also obtained using a Rigaku PIC-10C. IR studies were carried out using a Perkin Elmer 1600 FT–IR spectrophotometer. The contents of Na, K, and Mo in the samples were measured with an Hitachi 180-80 atomic absorption spectrometer using the 5890.0 Å line for

Na, the 7664.9 Å line for K, and the 3132.6 Å line for Mo. The contents of Mo^{5+} were determined by using the method of Choain and Marrion (13).

RESULTS

Preparation of Hydrated Potassium Bronzes

Schöllhorn *et al.* (7) reported that complete exchange of Na^+ in hydrated sodium molybdenum bronze with other alkali ions in the solution was observed at room temperature after several hours in most cases. Thomas *et al.* (10) obtained the exchanged samples by shaking a reaction mixture for 24 h. Here we studied the rate of ion exchange. The Na/Mo and K/Mo ratios of the exchanged samples with treatment times are shown in Table 1. Na^+ ions were exchanged by K^+ ions within 30 s for HyNa–AD and 10 min for HyNa–VD, respectively. This indicates that the exchange between Na^+ ions and K^+ ions takes place very quickly.

The samples exchanged by K^+ ions gave three kinds of XRD patterns as shown in Fig. 1. Figure 1A is the XRD pattern of the exchanged sample with the inter layer spacings of $d_{020} = 11.37$ Å immediately after filtration. This is labeled HyK–AD. Figures 1B and 1C are those with $d_{020} = 10.57$ and 9.36 Å, respectively. We call the former HyK–H2 and the latter HyK–H1. The chemical and TG results are shown in Table 2. According to the results, HyK–H2 possesses two hydrate waters per one K^+ ion and HyK–H1 possesses one hydrate water per one K^+ ion. The composition of HyK–AD, HyK–H2, and HyK–H1 are $\text{K}_{0.23}(\text{H}_2\text{O})_n\text{MoO}_{3.00}$ ($n \geq 0.65$), $\text{K}_{0.23}(\text{H}_2\text{O})_{0.43}\text{MoO}_{3.00}$, and $\text{K}_{0.23}(\text{H}_2\text{O})_{0.27}\text{MoO}_{3.00}$, respectively. HyK–H2 was obtained by leaving HyK–AD in air more than overnight. But, it is very difficult to obtain only the HyK–H1 phase in a reliable way. When HyNa–AD was used as the starting material and suspended for a long period, HyK–H1 can be obtained, but not with reproducibility. When HyK–AD was heated in nitrogen or in air, HyK–H1 was sometimes

TABLE 1
The Ratio of Na/Mo and K/Mo of the Exchanged Samples

Treatment time	Starting material			
	HyNa–AD		HyNa–VD	
	Na/Mo	K/Mo	Na/Mo	K/Mo
As prepared	0.23	0.00	0.23	0.00
30 s	0.01	0.22	0.22	0.00
10 min	0.00	0.22	0.01	0.22
1 h	0.00	0.22	0.00	0.22
4 h	0.00	0.22	0.00	0.22
8 h	0.00	0.22	0.00	0.22
24 h	0.00	0.22	0.00	0.22

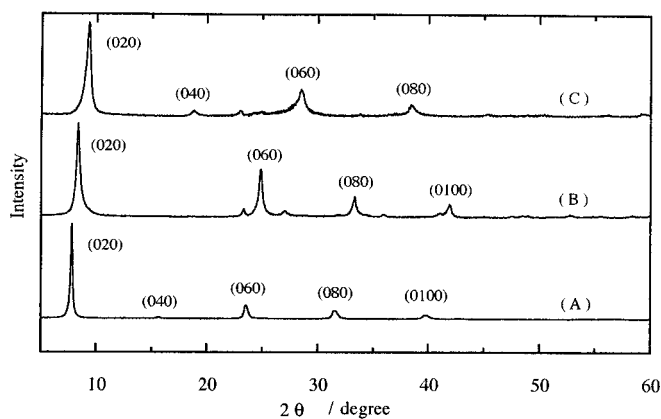


FIG. 1. XRD patterns of (A) HyK-AD, (B) HyK-H2, and (C) HyK-H1.

obtained under 573 K, but also not reproducibly. We are currently trying to establish a more rigorous protocol for the HyK-H1 synthesis.

Figure 2 shows the TG-DTA curve of HyK-H2 in air. Two endothermic peaks at 342 and 817 K and an exothermic peak at 551 K were observed. The endothermic peak at 342 K was accompanied by a weight loss (4.6%) which corresponded to dehydration. The gradual decrease in weight (0.4%) took place up to about 455 K without a clear DTA peak. This suggests the removal of protons and any remaining coordinated water. The exothermic peak at 551 K was accompanied by a weight gain (0.7%). This suggests the uptake of oxygen in air and an accompanying phase transformation of the sample. The exothermic peak at 817 K showed no weight change. This corresponds to the melting point of samples. There is no large difference in the DTA behavior for HyK-H2 and HyK-H1, except the difference in the weight decrease at low temperature. Figure 3 shows the TG-DTA curve of HyK-H2 in nitrogen. Also, the endothermic peak was accompanied by a weight loss (4.8%) which appeared at 342 K. The weight

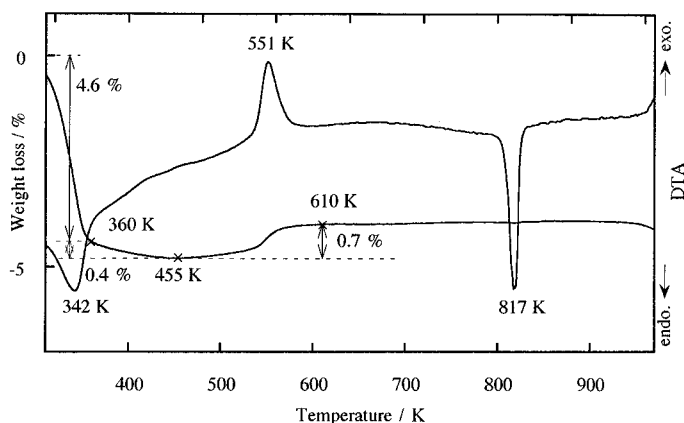


FIG. 2. TG-DTA curves of HyK-H2 in air.

decreases gradually between the temperatures of 382 and 636 K without any clear peak. This suggests the removal of protons and remaining coordinated water as in the case of measurement in air. The exothermic peak appeared at 621 K with no weight change, suggesting a phase transformation. Three endothermic peaks appeared at around 850 to 890 K, indicative of a partial melting of the sample.

Figure 4 shows IR spectra of HyK-H2 and HyK-H1, which are very similar. Both samples are dark blue in color, and intensity of their IR bands is very weak. HyK-H2 and HyK-H1 give weak, broad bands at 3555 and 3445 cm^{-1} . Also, weak bands appear at around 1630 cm^{-1} . This is attributed to hydrate water molecules. HyK-H2 shows bands at 953 and 575 cm^{-1} while those of HyK-H1 are at 953 and 581 cm^{-1} . The band at 953 cm^{-1} is assigned to a Mo=O double bond of terminal oxygen of the MoO_6 octahedra, and those at 575 and 581 cm^{-1} , to a Mo-O single bond. No significant difference was observed between the bands of HyK-H2 and HyK-H1. A small band appeared at around 1005 cm^{-1} . As reported previously for

TABLE 2
Results of Chemical and TG Analysis of HyK-AD, HyK-H2, and HyK-H1

	Mo (%)	K (%)	x	H ₂ O (%)	H ₂ O/K ⁺	H ⁺
HyK-AD	58.08 (1.00)	5.16 (0.23)	0.23	7.10 (0.65)	2.83	0.03
HyK-H2	59.63 (1.00)	5.54 (0.23)	0.23	4.60 (0.43)	1.87	0.03
HyK-H1	59.72 (1.00)	5.50 (0.23)	0.23	2.98 (0.27)	1.18	0.03

Note. HyK-AD, $\text{K}_{0.23}(\text{H}_2\text{O})_n\text{MoO}_{3.00}$ ($n \geq 0.65$); HyK-H2, $\text{K}_{0.23}(\text{H}_2\text{O})_{0.43}\text{MoO}_{3.00}$; HyK-H1, $\text{K}_{0.23}(\text{H}_2\text{O})_{0.27}\text{MoO}_{3.00}$.

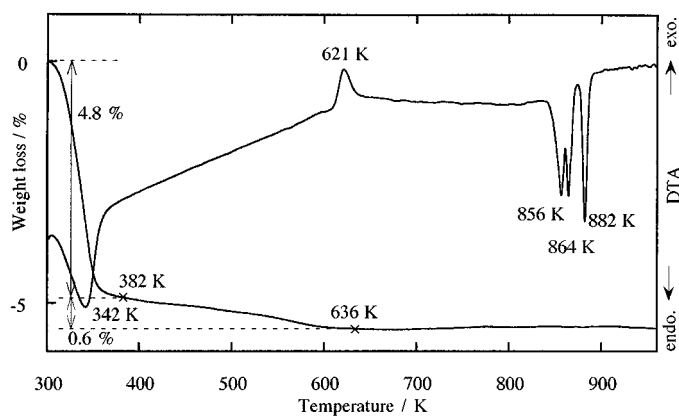


FIG. 3. TG-DTA curves of HyK-H2 in nitrogen.

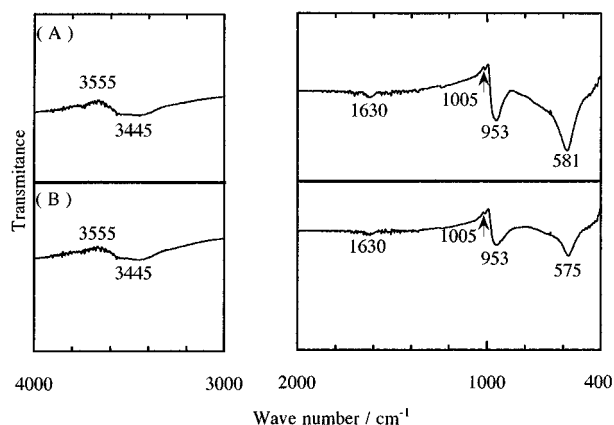


FIG. 4. IR spectra of (A) HyK-H1 and (B) HyK-H2.

(11), when a small amount of protons was introduced into the hydrated sodium bronzes, a small band also appeared at around 1005 cm^{-1} . Type I hydrogen bronze shows the typical IR band at around 1005 cm^{-1} , which appeared when protons were introduced into the intrasite between oxygens of MoO_6 octahedra (14). This suggests that the proton is introduced into the intrasite of hydrated potassium bronzes as in the case of Type I hydrogen bronze.

According to NMR results (15), the presence of protons was confirmed in HyK-AD, HyK-H2, and HyK-H1, but was not determined quantitatively. TG results in the air atmosphere shows the gradual weight decreases of 0.4% from 360 to 455 K and an increase of 0.7% upto 610 K. In the case of nitrogen atmosphere, the weight also decreases gradually by 0.6% from 382 to 636 K. The behavior of the weight decreases in both cases is very similar to the result of the Type I hydrogen bronze (14). Therefore, it is assumed that these gradual weight decreases result from the removal of protons. That is, the protons present in the bronze react with lattice oxygen to produce water molecules. The mass balance would say that not all the weight gain can be accounted for by oxygen lost in the deprotonation process, some net oxidation must also occur. As the removal and recombination occurred simultaneously, the weight changes are overlapped. Therefore, the precise weight loss due to proton removal can be obtained from the TG results by treating in nitrogen. The weight loss was 0.6% and corresponded to 0.03 mol of protons. This suggests that 0.03 mol of protons are included in HyK-H2 as impurities.

DISCUSSION

Ideal Composition of Hydrated Potassium Bronzes

The results of the chemical analysis are shown in Table 2. The quantity of the hydrate water was obtained from TG results from treatment in nitrogen atmospheres. The K^+/Mo ratio in HyK-AD, HyK-H2, and HyK-H1 is 0.23.

The $\text{H}_2\text{O}/\text{K}^+$ ratio is 2.83 for HyK-AD, 1.87 for HyK-H2, and 1.18 for HyK-H1. As has been reported (11) for hydrated sodium bronzes, that the ideal value of Mo^{5+} is $x = 0.25$, which consists of $[\text{MoO}_3]^{0.25-}$ layers. NMR and IR results prove the presence of a small amount of protons. According to TG results and chemical analysis, the bronzes include 0.03 mol of protons and the composition is $\text{K}_{0.23}(\text{H}_2\text{O})_n(\text{H})_{0.03}\text{MoO}_{3.00}$ ($n \geq 0.65$) for HyK-AD, $\text{K}_{0.23}(\text{H}_2\text{O})_{0.43}(\text{H})_{0.03}\text{MoO}_3$ for HyK-H2, and $\text{K}_{0.23}(\text{H}_2\text{O})_{0.27}(\text{H})_{0.03}\text{MoO}_3$ for HyK-H1. Therefore, an ideal composition of HyK-AD, HyK-H2, and HyK-H1 may be presented as $[\text{K}(\text{H}_2\text{O})_n]_{0.25}\text{MoO}_3$ ($n \geq 2.6$), $[\text{K}(\text{H}_2\text{O})_2]_{0.25}\text{MoO}_3$, and $[\text{K}(\text{H}_2\text{O})]_{0.25}\text{MoO}_3$, respectively.

K-H2 (Six-Coordination Type) and K-H1 (Eight-Coordination Type)

The observed d values, the calculated d values, and the indexing of HyK-AD, HyK-H2, and HyK-H1 are shown in Tables 3–5, respectively. Orthorhombic unit-cell parameters of HyK-AD, HyK-H2, and HyK-H1 are calculated from the X-ray results as shown in Table 6. There is a difference in b among HyK-AD, HyK-H2, and HyK-H1. On the other hand, there is no large difference in a and c . This suggests that the unit cells of HyK-AD and HyK-H2 expand along b axis as the orthorhombic structure. These results also suggest that the hydrated K^+ ions can be included between the terminal oxygens of MoO_6 octahedra of MoO_3 layers and the location in HyK-AD and HyK-H2 may be different from that in HyK-H1. A measure of whether a guest ion can penetrate into the MoO_3 layers should depend on an interlayer spacing. The value of d_{020} indicates a characteristic interlayer spacing. The d_{020} values of HyK-AD, HyK-H2, and HyK-H1 are shown in Table 7; d_{020} values of MoO_3 , HyNa-AD, and HyNa-VD are also shown. The d_{020} values of the hydrated bronzes are larger than those of the host sample, MoO_3 .

TABLE 3
Indexing of the X-Ray Powder Diffraction Pattern of HyK-AD,
 $\text{K}_{0.23}(\text{H}_2\text{O})_n\text{MoO}_{3.00}$ ($n \geq 0.65$)

d (Å) calc	d (Å) obs	h	k	l	I/I_0 obs	2θ obs
11.354	11.35	0	2	0	100	7.780
5.677	5.69	0	4	0	2	15.560
3.785	3.79	0	6	0	16	23.460
3.746	3.74	0	0	1	9	23.740
3.594	3.60	1	2	0	3	24.700
3.557	3.56	0	2	1	2	24.980
2.839	2.84	0	8	0	10	31.460
2.271	2.27	0	10	0	5	39.660
1.894	1.89	2	0	0	1	48.000
1.873	1.88	0	0	2	1	48.380
1.690	1.69	2	0	1	1	54.220

TABLE 4
Indexing of the X-Ray Powder Diffraction Pattern of HyK–H2,
 $\text{K}_{0.23}(\text{H}_2\text{O})_{0.43}\text{MoO}_{3.00}$

d (Å) calc	d (Å) obs	h	k	l	I/I_0 obs	2θ obs
10.752	10.67	0	2	0	100	8.36
5.376	5.37	0	4	0	6	16.48
3.811	3.81	1	1	0	9	23.32
3.581	3.58	0	6	0	52	24.86
3.300	3.30	0	2	1	6	27.00
2.688	2.69	0	8	0	22	33.32
2.492	2.51	0	6	1	2	35.78
2.214	2.21	1	5	1	4	40.86
2.150	2.15	0	10	0	15	41.90
2.124	2.14	0	8	1	4	42.24
2.033	2.01	1	9	0	2	45.00
1.906	1.86	2	2	0	3	48.96
1.734	1.73	0	0	2	4	52.72

($d_{020} = 6.92$ Å) (16). This means that an expansion of the interlayer spacing takes place by introducing the guest cations. The degree of the expansion, Δd , is obtained from the observed d_{020} value by subtracting d_{020} of MoO_3 . The Δd is summarized in Table 7.

The Δd of the VD type of hydrated alkali bronzes is plotted against ionic radius (17) as shown in Fig. 5. Though ionic radius of Rb^+ and Cs^+ is larger than that of Li^+ and Na^+ , the interlayer expansion by insertion of Rb^+ and Cs^+ is smaller than that of Li^+ and Na^+ . Figure 5 shows clearly the presence of two groups. One is a group of the six-

TABLE 5
Indexing of the X-Ray Powder Diffraction Pattern of HyK–H1,
 $\text{K}_{0.23}(\text{H}_2\text{O})_{0.27}\text{MoO}_{3.00}$

d (Å) calc	d (Å) obs	h	k	l	I/I_0 obs	2θ obs
9.321	9.36	0	2	0	100	9.44
4.661	4.66	0	4	0	10	19.02
3.830	3.84	1	0	0	5	23.16
3.614	3.64	0	1	1	3	24.44
3.543	3.56	1	2	0	3	25.02
3.169	3.18	0	3	1	3	28.08
3.107	3.11	0	6	0	38	28.70
2.959	2.96	1	4	0	3	30.14
2.629	2.64	1	1	1	2	33.94
2.442	2.45	1	3	1	2	36.66
2.330	2.33	0	8	0	16	38.66
1.991	1.98	1	8	0	3	45.74
1.916	1.91	2	0	0	2	47.52
1.876	1.87	2	2	0	2	48.56
1.864	1.87	0	10	0	2	48.78
1.807	1.81	0	2	2	3	50.40
1.806	1.80	0	9	1	3	50.68
1.676	1.67	1	10	0	1	54.78
1.660	1.66	1	0	2	1	55.40

TABLE 6
Orthorhombic Unit-Cell Parameters of HyK–AD, HyK–H2,
and HyK–H1

Crystal system	HyK–AD (Å)	HyK–H2 (Å)	HyK–H1 (Å)
	Orthorhombic	Orthorhombic	Orthorhombic
a	3.78(8)	3.87(3)	3.83(1)
b	22.70(8)	21.50(3)	18.64(2)
c	3.74(6)	3.46(9)	3.68(4)

Note. ESDs are very high for HyK–AD and HyK–H2, in fact one would conclude that HyK–AD is tetragonal.

coordinate type (called Co(6)) to which Li and Na belong, and the other, that of the eight-coordinate type (called Co(8)) to which Rb and Cs belong. According to Cotton and Wilkinson (17), hydrated radii of Li^+ and Na^+ are also larger than those of Rb^+ and Cs^+ . For VD-type bronzes, hydrated lithium and sodium bronzes have two hydrate water molecules, while hydrated rubidium and caesium bronzes have one hydrate water molecule. The hydration energy of Li^+ and Na^+ is larger than that of Rb^+ and Cs^+ (17). In the Co(6) group, the hydration energy is large enough so that an alkali ion can link two hydrate waters. The alkali metal ion is located in the center of four terminal oxygens of MoO_6 octahedra and two oxygens of two hydrate waters are attached at both sides of the alkali ion as shown in Fig. 6A. In the Co(8) group, though the ionic radius of Rb^+ and Cs^+ is larger than that of Li^+ and Na^+ , the expansion of hydrated rubidium and caesium bronze is smaller than that of hydrated lithium and sodium bronze. So it is reasonable to consider that the eight coordination is closely packed, compared with the six coordination. The alkali ion is located in the body center of eight terminal oxygens of MoO_6 octahedra. The hydration energy is so small that this group of alkali ions have one hydrate water. Therefore, alkali ions such as Rb^+ and Cs^+ can occupy the

TABLE 7
Interlayer Spacing, d_{020} , of the Hydrated Sodium and
Potassium Molybdenum Bronzes

	MoO_3	HyNa–AD	HyNa–VD	HyK–AD	HyK–H2	HyK–H1
d (Å)	6.92	11.30	9.54	11.35	10.67	9.36
Δd (Å) ^a	—	4.38	2.62	4.43	3.75	2.44
Schöllhorn (7)		11.41			10.72 ^b	
Thomas (10)		11.48	9.63	11.17	10.86 ^c	9.2

^a $\Delta d = d_{020}(\text{hydrated bronze}) - d_{020}(\text{MoO}_3)$.

^b Named HyK–AD.

^c Named HyK–AD, but not confirmed.

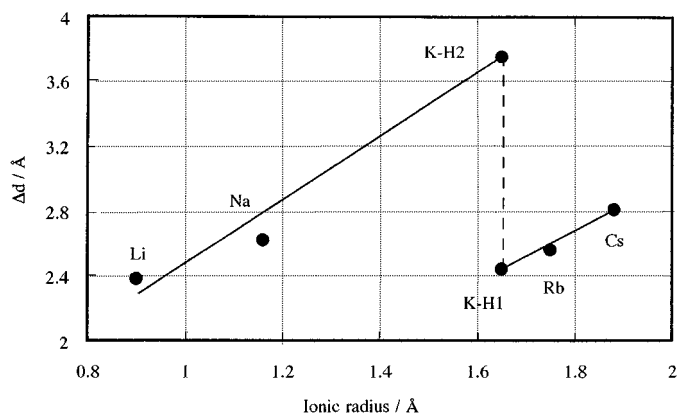


FIG. 5. The relation between ionic radius and Δd of the hydrated alkali bronzes.

center of eight terminal oxygens, and one hydrate water may be located in the unit next to the unit occupied by the alkali ion, as shown in Fig. 6B. K^+ ion has a medium hydration energy and hydrated radius. Therefore, HyK-VD can possess two types. The observed Δd of K-H2, which has two hydrate waters, just falls on the line of Rb and Cs. This result

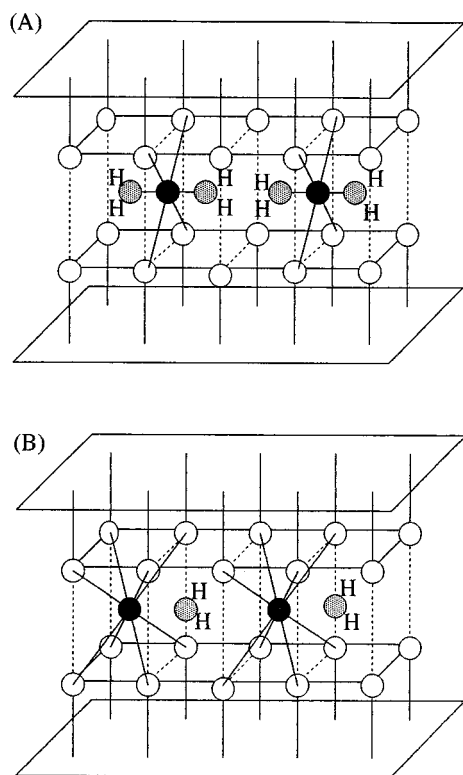


FIG. 6. Models of (A) six- and (B) eight-coordination types of the hydrated alkali bronzes.

clearly proves that there are two types of HyK-VD. That is, K-H2 belongs to the six-coordination type which has two hydrate waters, and K-H1 belongs to the eight-coordination type which has one hydrate water.

As mentioned previously, it is not easy to obtain HyK-H1. Possible reasons for this may depend on the hydration energy, the stereochemistry of the hydrated ion, the interaction power between the hydrated ion and terminal oxygens of MoO_6 octahedra, etc. In the case of the eight-coordination type of hydrated bronzes, such as hydrated rubidium and caesium bronzes, the protons in intrasites affect the ion exchange (18). Therefore, it can be considered that the proton may also affect the preparation of HyK-H1. This is not yet confirmed.

Preparation of Blue Potassium Bronze, $K_{0.3}MoO_3$

The result by heat treatment in nitrogen has been reported in (5). This is briefly summarized below. Figure 7 shows the XRD patterns of the samples heated in nitrogen at 573, 653, and 773 K. This shows the change from the composition of $K_{0.23}MoO_3$ which is isomorphous with the K-H1 structure to the blue potassium bronze, $K_{0.3}MoO_3$, and MoO_3 . As shown in Fig. 3, the transition takes place at 621 K and shows that the blue potassium bronze, $K_{0.3}MoO_3$, is obtained. According to Ramanujachary *et al.* (2), $K_{0.3}MoO_3$ was prepared at around 823 K by the fused method. Manthiram *et al.* (12) obtained $K_{0.30}MoO_3$ at 623 ~ 773 K. Our method is lower than the method by Ramanujachary *et al.* (2) by about 200 K and also lower than the method by Manthiram *et al.* (12). Moreover, $K_{0.3}MoO_3$ was obtained in solid state not through the fused state. This is a new method for preparing $K_{0.30}MoO_3$ at low temperature. This method includes a small amount of

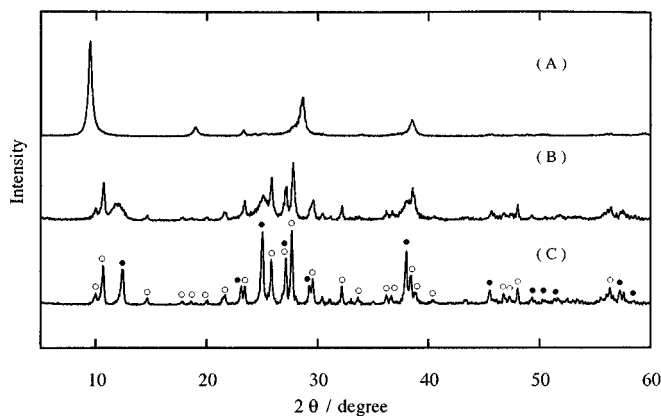
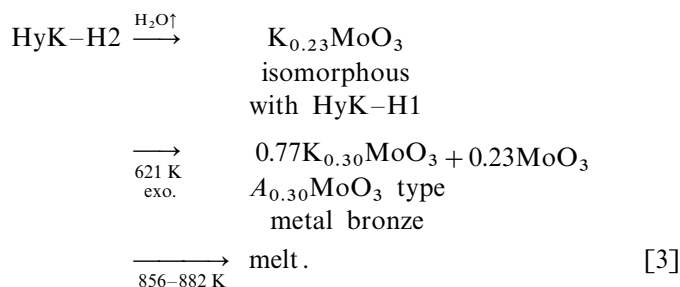


FIG. 7. XRD patterns of the samples heated in nitrogen. The K-H1-like structure heated at (A) 573 K, and the sample heated at (B) 653 and (C) 773 K: \circ , $K_{0.3}MoO_3$; \bullet , MoO_3 .

MoO₃ as an impurity. The process is shown in the following equation.



In order to obtain single phase of K_{0.30}MoO₃, it is necessary to remove MoO₃. We tried to obtain the single phase by controlling the amount of potassium ion in the hydrated potassium bronze and succeeded in reducing the amount of MoO₃, but could not remove it completely. Detailed results will be reported elsewhere.

Decomposition in Air

HyK-H2 heated in air at 423, 573, and 773 K were observed by XRD, which is shown in Fig. 8. The XRD patterns of the sample heated at 423 K shows the HyK-H1-like structure although the X-ray peaks are small and broad. The samples heated at 573 and 773 K give the XRD patterns attributed to K₂Mo₄O₁₃ and MoO₃. The peaks of the sample heated at 773 K are sharp. According to the X-ray result, the exothermic peak at 551 K corresponds to the decomposition of the HyK-H1-like structure with the composition of K_{0.23}MoO₃ to K₂Mo₄O₁₃ and MoO₃.

According to chemical analysis, the content of K⁺ of the sample heated at various temperatures was constant, but that of Mo⁵⁺ decreased gradually with the sample heated at 573 K in air being completely oxidized. The sample heated above 817 K and then cooled to room temperature also clearly yields an XRD pattern corresponding to a mixture of K₂Mo₄O₁₃ and MoO₃. The change by heating in air is summarized by

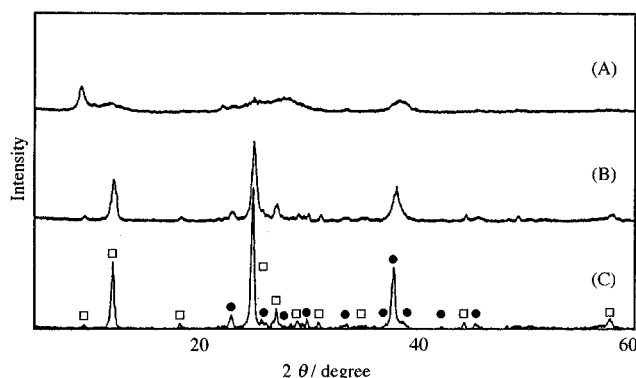
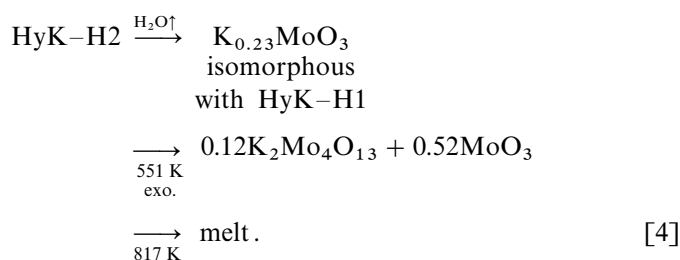


FIG. 8. XRD patterns of the samples heated in air. The K-H1-like structure heated at (A) 423 K, and the sample heated at (B) 653 and (C) 773 K: □, K₂Mo₄O₁₃; ●, MoO₃.

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