Journal of Solid State Chemistry **159,** 87–93 (2001)
doi:10.1006/jssc.2001.9135, available online at http://www.idealibrary.com on IDEAL®

Direct Synthesis of Hydrogen Coinserted Hydrated Sodium and Potassium Molybdenum Bronzes: Their Characterization and Selective Preparation of Purple, Blue, and Red Molybdenum Bronzes

Noriyuki Sotani,[1] Tomoyuki Manago, Takashi Suzuki, and Kazuo Eda

Department of Chemistry, Faculty of Science, Kobe University, Tsurukabuto, Nada, Kobe 657-8501, Japan

Received September 25, 2000; in revised form February 14, 2001; accepted March 5, 2001; published online May 11, 2001

We succeeded in synthesizing the hydrogen coinserted hydrated potassium molybdenum bronzes (HKBz) with the 8- and 6-coordination structures by a direct new reduction method. By this method, the 8-coordination type was obtained. According to NMR results, the behavior of protons in the 8-coordination type was different from those in the 6-coordination type. We obtained the single phase of purple sodium molybdenum bronze when hydrogen coinserted hydrated sodium bronze (HNaBz) controlled the content of hydrogen, and sodium was heated in nitrogen. Also, we obtained the blue and red potassium bronzes by heating HKBz and controlling the contents of hydrogen and potassium. © 2001 Academic Press

Key Words: **direct synthesis; $K_2S_2O_4$ solution; Raman spectroscopy; hydrogen coinserted hydrated sodium and potassium molybdenum bronze; proton NMR; purple bronze; blue bronze; red bronze.**

INTRODUCTION

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

$$xA^+ + xe + yH_2O + MoO_3 \rightarrow [A^+(H_2O)_{y/x}]_x[MoO_3]^{x^-}, \qquad [1]$$

where A is Li, Na, K, Rb, and Cs. MoO_3 must be reduced before any of the guest cations are inserted. The hydrated sodium bronze, $[Na^+(H_2O)_{y/x}]_x[MoO_3]^{x^-}$, is easily obtained using sodium dithionate, $Na_2S_2O_4$, which is a conventional reducing reagent for MoO_3 (1–4). The ideal x value of the hydrated sodium bronze is 0.25. When the reduction is strong enough, the proton is inserted to compensate the electric charge to form $[Na(H_2O)_{y/x}]_x[H_zMoO_3]$ (5, 6). Other hydrated alkali bronzes are obtained only by the cation exchange from hydrated sodium bronze in ambient electrolyte solution, because there is no useful alkali reagent for reduction except $Na_2S_2O_4$.

It has been reported (7) that two kinds of hydrated potassium bronzes exist. One is the 6-coordination structure (HyK–H2) and the other is the 8-coordination structure (HyK–H1). Figure 1 shows the models of the 6- and 8-coordination structures. In the case of the 6-coordination structure, the K^+ ion with two hydrate waters is located in the center of four terminal oxygens of MoO_6 octahedra. While in the 8-coordination structure, the K^+ ion is located in the center of eight terminal oxygens of MoO_6 octahedra, and the one hydrate water is located in the next unit. However, it is very difficult to synthesize the HyK–H1 type by the ion exchange method at any time, which may depend on the synthesis condition. We could not establish the synthesis condition by this time. Recently, we tried to establish the synthesis condition for the 6-coordination type of hydrated potassium bronzes by direct reduction method using $K_2S_2O_4$ solution as a reducing reagent. Since $K_2S_2O_4$ was not available in the market, we obtained the $K_2S_2O_4$ solution as described in the Experimental section, though ultimately a solid phase of $K_2S_2O_4$ could not be obtained. Using this $K_2S_2O_4$ solution, we were able to synthesize the 6-coordination hydrated potassium bronze. This was a first success, though the 6-coordination type necessarily coinserted hydrogens.

Eda *et al.* (8) prepared the hydrogen coinserted hydrated sodium bronze, $Na_{0.25}(H_2O)_yH_{0.21}MoO_3$, by using hydrogen bronze as the host material. Recently, using an oxygen-free nitrogen-vacuum line system, we directly synthesized hydrogen coinserted sodium and potassium hydrated molybdenum bronzes with various hydrogen contents by controlling the amount of reducing reagent according to

$$MoO_3 + xA^+ + yH_2O + zH^+ \rightarrow [A^+(H_2O)_{y/x}]_xH_z^+[MoO_3]^{(x+z)-}, \qquad [2]$$

---

[1] To whom correspondence should be addressed. E-mail: sotani@kobe-u.ac.jp.

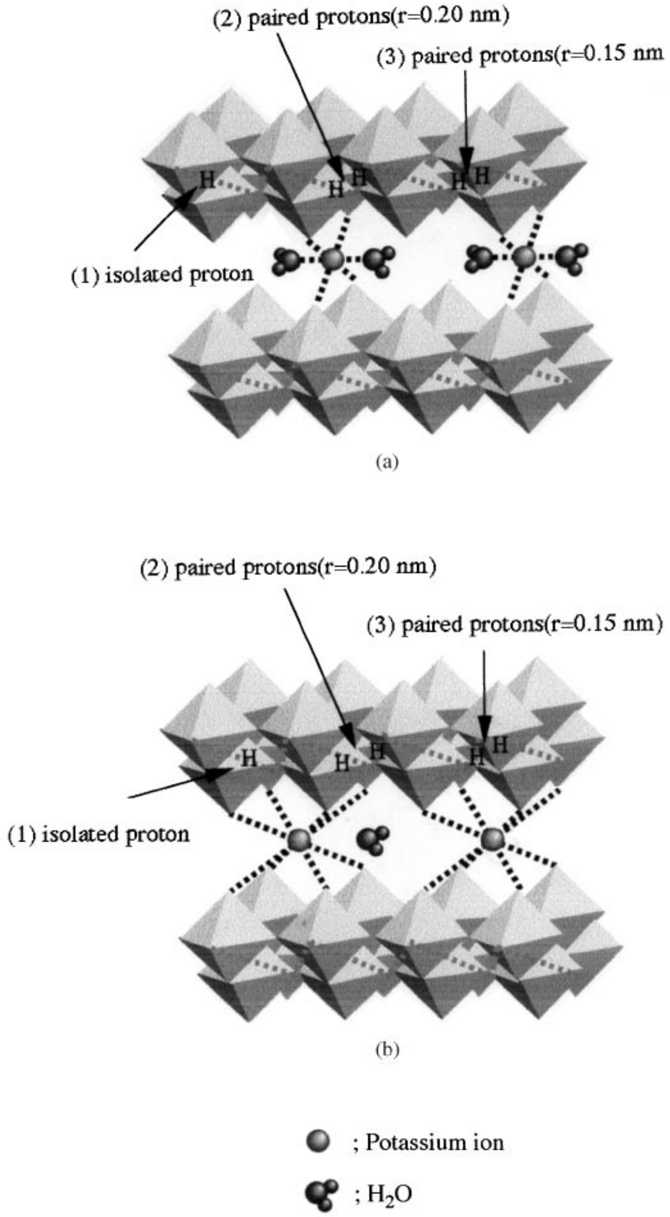

FIG. 1. Model of the 6- and 8-coordination structures: available proton sites in (a) HKBz-6 and (b) HKBz-8; (1) shows the isolated fixed proton, (2) shows the paired protons with $r = 0.15$ nm, and (3) shows the paired protons with $r = 0.20$ nm.

where A is Na and K. Moreover, we could synthesize hydrogen coinserted anhydrous potassium bronze, AHKBz-8, at any time by treating the 6-coordination type under vacuum, which was identical with the 8-coordination type (HyK–H1). We will report this in detail.

We already reported (9–12) that alkali metal bronzes were obtained at about 600 K by about 200 K lower than the usual fused method when hydrated alkali molybdenum bronzes were used as a starting material. Unfortunately, a very small amount of molybdenum oxide was mixed as an impurity. But, at the same time, it was suggested that by controlling the content of alkali/hydrogen ratio, a single phase of alkali metal bronze could be obtained. Therefore, we have succeeded in controlling the content of alkali metal/hydrogen ratio by using the direct preparation method, and we have succeeded in obtaining the single phase. This will also be reported.

EXPERIMENTAL

Materials

Preparation of $K_2S_2O_4$ solution as a reducing reagent. As $K_2S_2O_4$ was not available in the market, we prepared the $K_2S_2O_4$ solution. Dithionate ion, $S_2O_4^{2-}$ is theoretically obtained, according to

$$CO_3^{2-} + 2SO_2 + H_2O \rightarrow 2HSO_3^- + CO_2\uparrow \qquad [3]$$

$$HSO_3^- + SO_2 + Zn \rightarrow Zn^{2+} + S_2O_4^{2-} + OH^-. \qquad [4]$$

To remove Zn^{2+} ions in the solution, KOH is introduced. $Zn(OH)_2$ is obtained, according to

$$Zn^{2+} + 2KOH \rightarrow 2K^+ + Zn(OH)_2\downarrow. \qquad [5]$$

Consequently, the precipitate is separated and the $K_2S_2O_4$ solution containing K^+ and $S_2O_4^{2-}$ ions is obtained.

Actually, $K_2S_2O_4$ solution was obtained by dissolving 10 g of K_2CO_3 in 40 ml distilled water at 298 K according to Eq. [3] and then cooled to about 283 K in an ice bath. SO_2 gas was bubbled into the solution with hard stirring by a magnetic stirrer. When the solution reached pH 3–4, SO_2 gas was stopped and 3.5 g of zinc powder was introduced immediately with mild stirring for about 1 min. The color of the solution changed from gray to grayish-white. Three moles KOH (about 20 ml) was introduced drop by drop until no precipitate took place. The solution with the

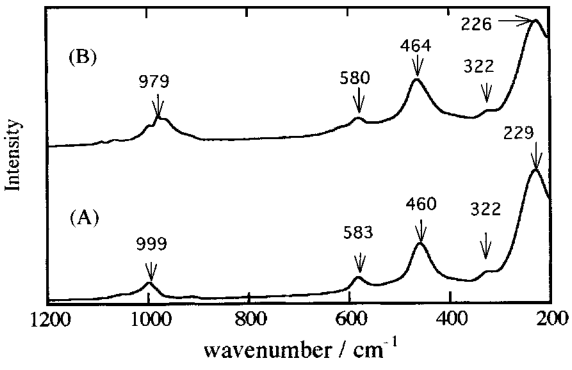

FIG. 2. Raman spectra of (A) $Na_2S_2O_4$ and (B) $K_2S_2O_4$ solution.

precipitate was separated into the supernatant solution and the precipitate by a centrifuge. The supernatant solution was observed by Raman spectroscopy. Figure 2 shows Raman spectra of the $Na_2S_2O_4$ solution and the $K_2S_2O_4$ solution obtained by the above method. The peaks of the $Na_2S_2O_4$ solution appeared at 999, 583, 460, 322, and 229 cm^{-1} due to the $S_2O_4^{2-}$ ion. The peaks of the synthesized $K_2S_2O_4$ solution appeared at 979, 580, 464, 322, and 226 cm^{-1}. The peaks are very similar to those of the $Na_2S_2O_4$ solution, though the peak at 979 cm^{-1} is broad and the wave number is rather low. The spectrum proved the formation of the $S_2O_4^{2-}$ ion. Therefore, this solution could be effective as the reducing reagent for direct synthesis of the hydrated potassium bronzes.

Direct preparation of hydrogen coinserted hydrated sodium and potassium bronzes. Hydrogen coinserted hydrated sodium and potassium bronzes were directly synthesized in an oxygen-free nitrogen-vacuum line system described in (13). Hydrogen coinserted hydrated potassium bronzes were prepared as follows-; 4 g of MoO_3 was suspended in 15 ml of distilled water and 25 ml of the $Na_2S_2O_4$ and $K_2S_2O_4$ solution was introduced at constant flow rate controlled by the pressure difference. The precipitate was suction filtrated, washed with distilled water, and dried in the vacuum system.

Measurements

Raman spectra were recorded on a Perkin–Elmer system 2000 RNIR FT-Raman spectrometer. Thermal gravimetric–differential thermal analysis (TG–DTA) studies were performed both in air and in nitrogen using a Mac Science TG DTA2000 with a heating rate of 10 $K min^{-1}$. X-ray diffraction (XRD) patterns of the samples were obtained using a Mac Science MXP3 X-ray diffractometer with Cu*Kα* radiation (40 KV, 35 mA). Proton NMR was detected at the liquid-nitrogen temperature (77 K) using a home-built NMR spectrometer operating at 11 MHz; absorption spectra were obtained by Fourier Transform of free induction decay (FID) signals. The contents of Na, K, and Mo were measured with a Hitachi 180-80 atomic absorption spectrometer using the 589.00 nm line for Na, the 766.49 nm line for K, and the 313.26 nm line for Mo. The total content of Mo^{5+} was determined by the redox titration method (14).

RESULT AND DISCUSSION

Direct Preparation of Hydrogen Coinserted Hydrated Sodium and Potassium Bronzes with the 6-Coordination Structure and Control of the Alkali Metal Content

Hydrogen coinserted hydrated sodium (HNaBz) and potassium (HKBz-6) with 6-coordination structure were directly prepared in the oxygen-free nitrogen-vacuum line, by changing the degree of reduction. Table 1 shows the contents of Na^+ or K^+, H^+, and Mo^{5+}/Mo. Figures 3 and 4 show XRD patterns of hydrogen coinserted sodium and potassium bronzes, respectively. A small amount of H_xMoO_3 (Hydrogen bronze Type II) phase began to appear at H^+ content of above 0.31 for HNaBz and 0.32 for

TABLE 1
Content of Na^+, K^+, H^+, and Mo^{5+} by Chemical Analysis

	Na^+/Mo	H^+/Mo	Mo^{5+}/Mo
HNaBz	(A) 0.24	0.17	0.41
	(B) 0.24	0.18	0.43
	(C) 0.25	0.26	0.51
	(D) 0.22	0.31	0.53
	(E) 0.19	0.47	0.66
	K^+/Mo	H^+/Mo	Mo^{5+}/Mo
HKBz-6	(A) 0.22	0.17	0.39
	(B) 0.25	0.23	0.48
	(C) 0.25	0.32	0.57
	(D) 0.18	0.92	1.10
	(E) 0.09	1.19	1.28

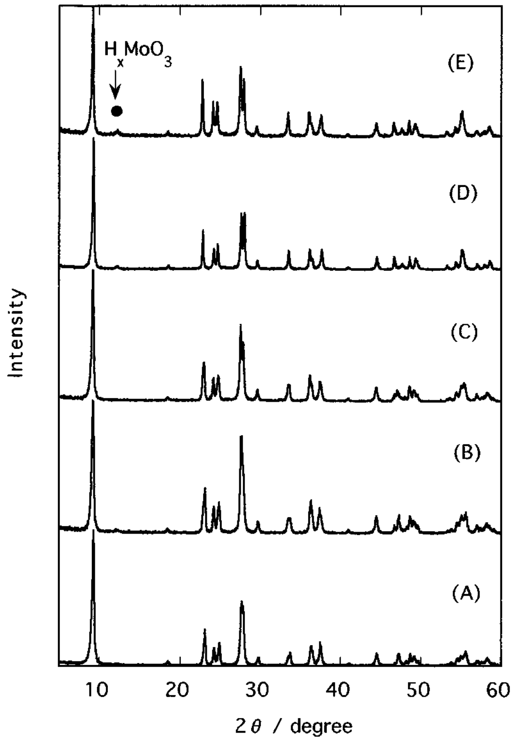

FIG. 3. XRD patterns of hydrogen coinserted hydrated sodium molybdenum bronzes with various hydrogen contents of H^+/Mo: (A) = 0.17, (B) = 0.18, (C) = 0.26, (D) = 0.31, and (E) = 0.47; (●) represents H_xMoO_3(Type II).

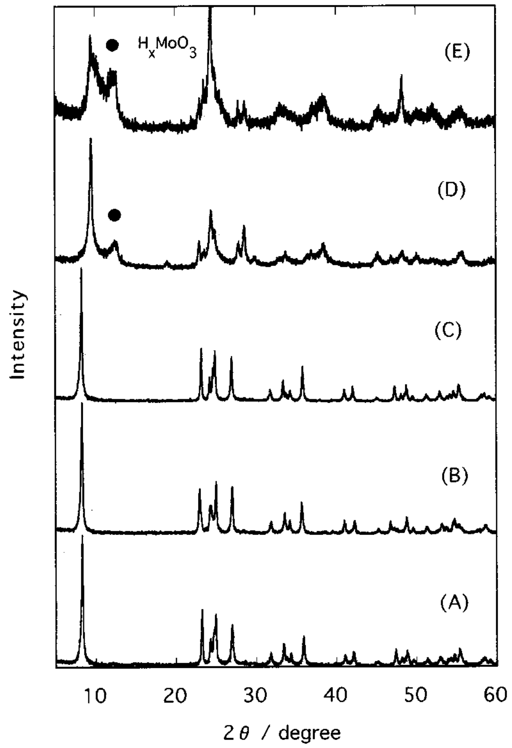

FIG. 4. XRD patterns of hydrogen coinserted hydrated potassium molybdenum bronzes with various hydrogen contents of H^+/Mo: (A) = 0.13, (B) = 0.19, (C) = 0.32, (D) = 0.92, and (E) = 1.19; (●) represents $HxMoO_3$(Type II).

HKBz-6. Na^+ and K^+ contents decreased to under 0.2, and the total reduction degree was over 0.6. In the case of hydrogen bronze, Type II phase began to appear above 0.4 of Mo^{5+}/Mo (15). The results of chemical analysis proved that the content of Na^+ and/or K^+ ions and hydrogens could be controlled by changing the degree of reduction.

Preparation of Hydrogen Coinserted Potassium Bronze with the 8-Coordination Structure

As mentioned previously (7), it is very difficult to obtain the 8-coordination type hydrated potassium bronze, Hyk–H1. However, the anhydrous hydrogen coinserted potassium bronze, *A*HKBz-8, with 8-coordination structure was obtained when HKBz-6 was dried under vacuum overnight. As shown in Fig. 5, the XRD pattern of *A*HKBz-8 with $d_{020} = 9.05$ Å gradually decreases, the peak with $d_{020} = 10.59$ Å due to HKBz-6 appears and gradually increases. Finally, the XRD pattern shows a single phase of HKBz-6. By leaving it in the glove box filled with water vapor, *A*HKBz-8 was changed to HKBz-6. By treating HKBz-6 under vacuum, it easily changed to *A*HKBz-8. This suggests that hydrate water plays an important role in changing from *A*HKBz-8 to HKBz-6. According to chemical analysis, the composition of *A*HKBz-8 and HKBz-6 was $K_{0.25}H_{0.23}MoO_3$ and $K_{0.25}H_{0.23}MoO_3 \cdot 0.5H_2O$, respectively. As *A*HKBz-8 can easily incorporate water vapor, it is very difficult to determine the contents of water. The XRD pattern with $d_{020} = 10.59$ Å agreed well with the pattern of the hydrated potassium bronze (HyK–H2) with two hydrate waters per one K^+ ion, which was obtained by the ion exchange method (7). The XRD pattern with $d = 9.05$ Å was similar to patterns of hydrated potassium bronze, HyK–H1, with one hydrate water per one K^+ ion in the 8-coordination structure (7), though it had no definite hydrate water. HyK–H1 with 8-coordination structure could not be obtained using the ion exchange method, but, by using the direct reduction method, the 8-coordination structure was obtained, though many hydrogens were inserted. This shows that the coinserted hydrogens is very effective in the 8-coordination structure. This is the new method for directly synthesizing hydrogen coinserted potassium bronzes with 8-coordination structures.

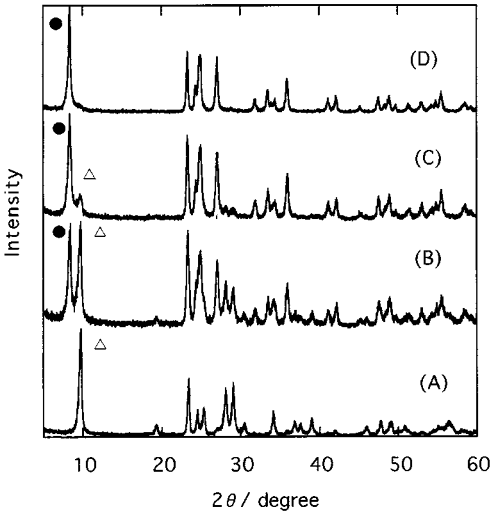

FIG. 5. Change in XRD patterns of *A*HKBz (anhydrous hydrogen coinserted potassium bronze) by standing in air. (A) *A*HKBz (8-coordination structure), and standing for (B) 30, (C) 60, and (D) 90 min (HKBz-6; 6-coordination structure); (●) represents 8-coordination and (△) represents 6-coordination.

PROTON BEHAVIOR

It has been reported (6) that NMR spectra of hydrated sodium bronze, HyNa, and hydrogen coinserted hydrated sodium bronze, HNaBz, which was obtained from hydrogen bronze, have three peaks—a central peak and two side peaks. The side peaks can be attributed to paired protons resulting in a Pake doublet (16, 17) and the central peak can be attributed to isolated protons resulting in a Gaussian line shape (18). According to the results, the spectrum of HyNa

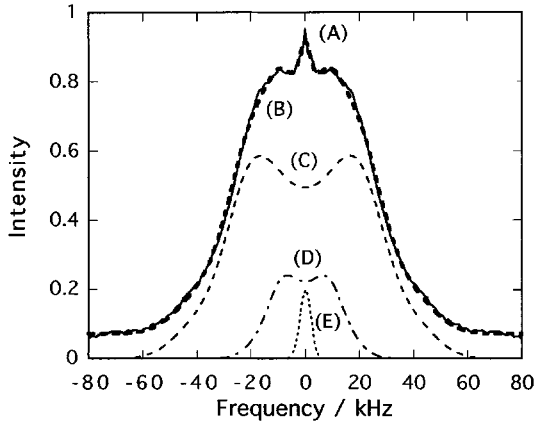

FIG. 6. NMR spectrum of HNaBz-6: (A) observed spectrum, (B) simulated curve, (C) two-spin system (H_2O), (D) two-spin system, and (E) the isolated immobile proton.

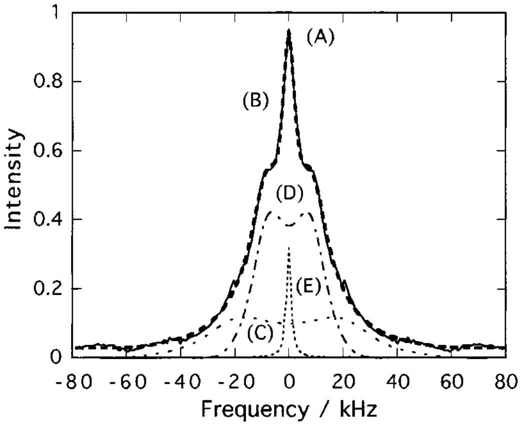

FIG. 8. NMR spectrum of HKBz-8 with 8-coordination structure: (A) observed spectrum, (B) simulated curve, (C) two-spin system(H_2O), (D) two-spin system, and (E) the isolated immobile proton.

consisted of a Pake doublet, D(f), and a Gaussian, G(f), while that of hydrogen coinserted hydrated sodium bronze, consisted of two Pake doublets, D_1(f) and D_2(f), and a Gaussian, G(f). NMR spectra of HNaBz-6, HKBz-6, and HKBz-8 are shown in Figs. 6–8, respectively. We, therefore, have tried to construct the simulated spectra for these observed spectra from two Pake doublets (D_1(f) and D_2(f) and a Gaussian (G(f)) as

$$Y(f) = aG(f) + bD_1(f) + cD_2(f). \qquad [6]$$

We successfully obtained simulated spectra as shown in Figs. 5–7, and they are best fitted to the observed spectrum. The detailed theoretical treatment is described in (15). Parameters, *a*, *b*, *c*, of Eq. [6] and proton–proton distance are shown in Table 2. The proton–proton distance, r_1, is suitable for the protons in H_2O. Therefore, the first Pake doublet results from the protons in H_2O (6, 16). The proton–proton distance, r_2, is 0.15 nm for HKBz-6 and 0.20 nm for HNaBz-6, respectively. HKBz-8, in which *A*HKBz-8 incorporates water, has a proton–proton distance, r_2, of 0.2 nm. In the case of hydrogen bronze, there are two available proton sites between the intralayer of MoO_6 octahedra. When protons are inserted, they can occupy one of the available sites depending on the condition. In this case, the proton–proton distance is 0.15 or 0.20 nm (15, 19). Therefore, r_2 agrees well with the intralayer proton–proton distance. As Na^+ and/or K^+ ions should take the interlayer sites, it is reasonable that the coinserted hydrogen occupied the intralayer sites, as shown in Fig. 1.

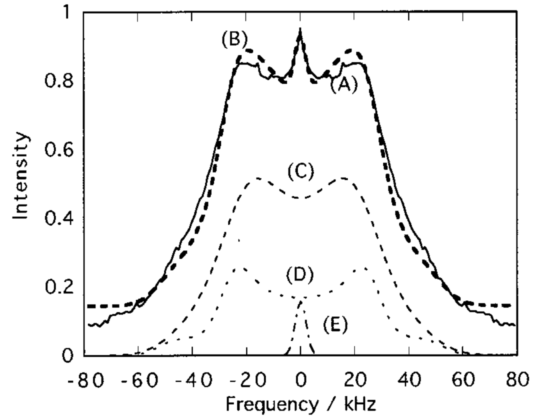

FIG. 7. NMR spectrum of HKBz-6 with 6-coordination structure: (A) observed spectrum, (B) simulated curve, (C) two-spin system (H_2O), (D) two-spin system, and (E) the isolated immobile proton.

Parameter *b* in Table 2 obtained from the simulated spectrum gives the ratio of hydrogens in hydrate waters to the total amount of hydrogens. Numerals in parentheses represent the number of protons. The values of HNaBz–6 and HKBz-6 agreed with those obtained by thermogravimetry, but the value of HKBz-8 was about one-half of the thermogravimetric results. Parameters *a* and *c* correspond to the protons in the intralayer sites. Compared to 6-coordination, HKBz-8 has more intrasite paired protons corresponding to *b*. Insertion of protons may depend on the location of the K^+ ion. As mentioned above, in the case of 8-coordination, the K^+ ion is located in the center of eight terminal oxygens of MoO_6 octahedra and one hydrate water occupies the next unit, as shown in Fig. 1. *A*HKBz-8 can easily incorporate water vapor, and once the K^+ ion takes the 8-coordination structure, it keeps the 8-coordination structure until hydrate water is contained enough to occupy the next unit to K^+ ion and to change the 6-coordination structure. Therefore, it may be reasonable that about half of the protons occupy the intralayer sites. The hydrogens in the 6-coordination structure are different from those in the 8-coordination. The 6-coordination structure

TABLE 2
Parameters of Eq. [6] and Proton–Proton Distance

	a (Gauss)	*b* (H_2O)	*c* (paired)	r_1/nm	r_2/nm	H_2O/Na or K[a]
$Na_{0.24}H_{0.18}MoO_30.47H_2O$ (HNaBz-6)	0.012 (0.01)	0.755 (0.85)	0.233 (0.26)	0.16	0.20	1.96 (1.71)[b]
$K_{0.25}H_{0.23}MoO_30.5H_2O$ (HKBz-6)	0.016 (0.02)	0.681 (0.84)	0.303 (0.37)	0.16	0.15	2.00 (1.68)[b]
$K_{0.25}H_{0.23}MoO_30.21H_2O$ (HKBz-8)	0.101 (0.06)	0.303 (0.20)	0.596 (0.39)	0.16	0.20	0.84 (0.40)[b]

Note. Numerals in parentheses represent the corresponding number of protons.

[a] Values obtained from thermogravimetric results.

[b] Represents the amount of water which corresponds to column *b*.

prefers to have stoichiometric two hydrate waters per one Na^+ and/or K^+ ion, but the hydrogens in the 8-coordination structure prefer to take the site in intralayer of MoO_3 sheets. This difference results from the location of the K^+ ion as shown in Fig. 1.

SELECTIVE PREPARATION OF ALKALI METAL BRONZES

Preparation of Purple Sodium Bronze

Figure 9 shows the TG–DTA curve of HNaBz ($Na^+/Mo = 0.25$ and $H^+/Mo = 0.26$) in nitrogen. The TG curve decreased by three steps. The first and second decreases corresponded to the dehydration. The last step was very small, accompanied by an exothermic peak at around 600 K, which corresponded to an irreversible transformation. According to XRD results, HNaBz shows its original structure before the exothermic peak and shows XRD patterns due to the purple bronze, $Na_{0.9}Mo_6O_{17}$, and a small amount of MoO_2 heated at 773 K. Figure 10 shows XRD patterns of HNaBz with various Na^+ and H^+ contents heated at 773 K in nitrogen. HNaBz with high hydrogen and low Na contents gave rather much MoO_2, while that with low hydrogen and high Na contents gave a very small amount of MoO_2. In the case of $H^+ = 0.26$ and $Na^+ = 0.25$, MoO_2 was not detected, as shown in Fig. 10. This suggests that a single phase of the purple bronze can be obtained by controlling the contents of hydrogen and the Na^+ ion.

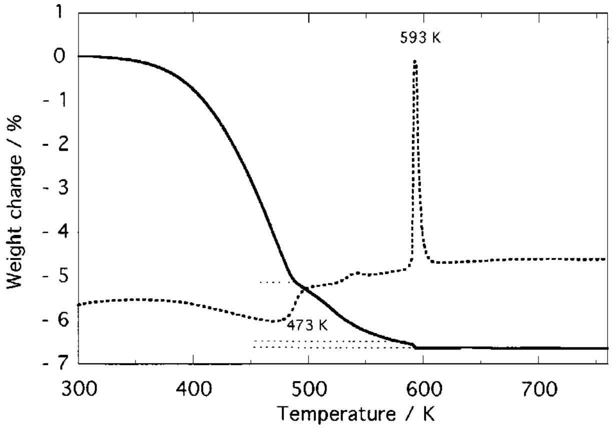

FIG. 9. TG–DTA curve of HNaBz-6 in nitrogen.

Selective Preparation of Blue and Red Potassium Bronzes

Figure 11 shows the TG–DTA curve of HKBz-6 ($K^+ = 0.25$ and $H^+ = 0.23$) in nitrogen. This is very similar

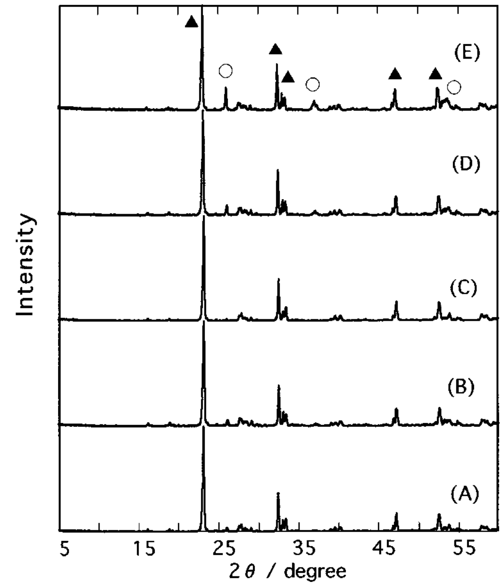

FIG. 10. XRD patterns of HNaBz-6 with various reduction states of (A) $Na^+ = 0.24$ and $H^+ = 0.17$, (B) $Na^+ = 0.25$ and $H^+ = 0.18$, (C) $Na^+ = 0.25$ and $H^+ = 0.26$, (D) $Na^+ = 0.22$ and $H^+ = 0.31$, and (E) $Na^+ = 0.19$ and $H^+ = 0.47$ heated in nitrogen at 773 K; (▲) represents purple bronze and (○) represents MoO_2.

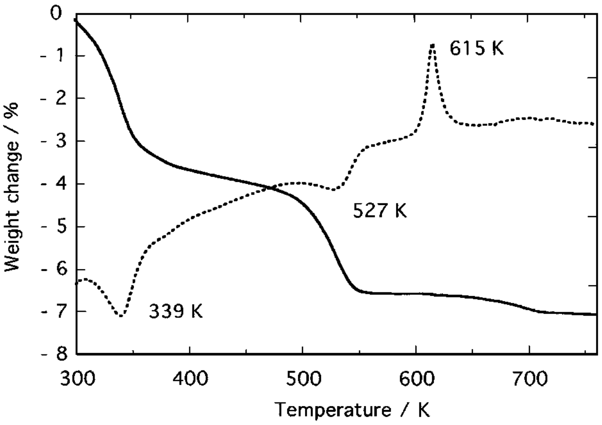

FIG. 11. TG–DTA curve of HKBz-6($K^+ = 0.25$ and $H^+ = 0.23$) in nitrogen.

to that of HNaBz. Figure 12 shows the XRD patterns of HKBz-6 with various K^+ and H^+ contents heated at 773 K in nitrogen. HKBz(B) with $K^+ = 0.25$ and $H^+ = 0.23$ gave the red potassium bronze, $K_{0.33}MoO_3$, and a small amount of MoO_2, while those (A and C) with K^+ less than 0.25 gave the blue potassium bronze, $K_{0.30}MoO_3$, and MoO_2.

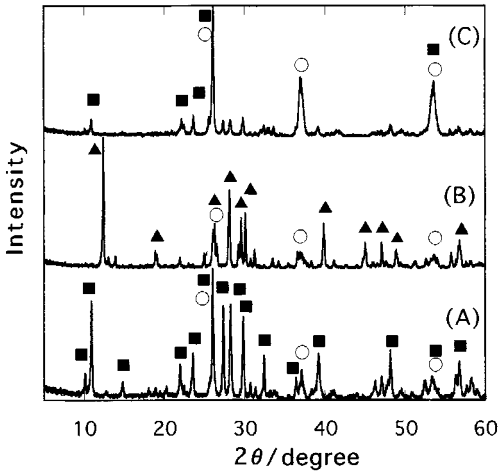

FIG. 12. XRD patterns of HKBz-6 with various reduction states of (A) $K^+ = 0.22$ and $H^+ = 0.17$, (B) $K^+ = 0.25$ and $H^+ = 0.23$, and (C) $K^+ = 0.99$ and $H^+ = 1.19$, heated in nitrogen at 773 K; (■) represents blue bronze, (▲) represents red bronze, and (○) represents MoO_2.

It is very interesting that the K^+ ion content controls the products; when HKBz contains K^+ ion content of 0.25, which is the maximum, the red potassium bronze results. On the other hand, when K^+ ion content in HKBz is less than 0.25, the blue potassium bronze results. The fact that the red bronze has more K^+ ions than the blue bronze supports this result. This is a newly found result. We can, therefore, selectively obtain the blue or red potassium bronze by controlling the amount of K^+. In both cases, if the hydrogen content is higher, more MoO_2 is prepared. It is clear that the amount of coinserted hydrogens controls the amount of K^+.

REFERENCES

1. R. S. Schollhorn, R. Kuhlman, and J. O. Besenhard, *Mater. Res. Bull.* **11,** 83 (1976).
2. S. Son, F. Kanamaru, and M. Koizumi, *Inorg. Chem.* **18,** 400 (1979).
3. T. Iwamoto, Y. Itoh, K. Ohkawa, and M. Takahashi, *Nippon Kagaku Kaishi* **1983,** 272 (1983).
4. D. Thomas and E. M. McCaron, III, *Mater. Res. Bull.* **21,** 945 (1986).
5. N. Sotani, K. Eda, and M. Kunitomo, *J. Solid State Chem.* **89,** 123 (1990).
6. M. Kunitomo, T. Kohmoto, Y. Fukuda, K. Eda, N. Sotani, and M. Kaburagi, *Phys. Lett. A* **199,** 103 (1995).
7. N. Sotani, T. Suzuki, K. Eda, M. Yanagi-ishi, S. Takagi, and F. Hatayama, *J. Solid State Chem.* **132,** 330 (1997).
8. K. Eda, F. Hatayama, M. Kunitomo, T. Kohmoto, and N. Sotani, *J. Mater. Chem.* **4,** 205 (1994).
9. K. Eda, K. Furusawa, F. Hatayama, S. Takagi, and N. Sotani, *Bull. Chem. Soc. Jpn.* **64,** 161 (1991).
10. N. Sotani, K. Eda, M. Yanagi-ishi, and S. Takagi, *Mater. Res. Bull.* **28,** 363 (1993).
11. N. Sotani, T. Miyazaki, K. Eda, and F. Hatayama, *J. Mater. Chem.* **7,** 2253 (1997).
12. K. Eda, T. Miyazaki, N. Sotani, F. Hatayama, and M. Nakagawa, *J. Solid State Chem.* **137,** 12 (1998).
13. T. Manago, Master's degree thesis, Kobe University, 1999.
14. C. Choain and F. Marion, *Bull. Soc. Chim. Fr.* **1963,** 212.
15. M. Kunitomo, K. Eda, N. Sotani, and M. Kaburagi, *J. Solid State Chem.* **99,** 395 (1992).
16. G. E. Pake, *J. Chem. Phys.* **16,** 327 (1948).
17. K. Ghoshray, B. Bandyopadyay, Mita Sen, A. Ghoshray, and N. Chatterjee, *Phys. Rev. B* **47,** 8277 (1993).
18. A. Abragam, "The Principals of Nuclear Magnetism," Oxford Univ. Press, London, 1961.
19. T. Fukumoto, Master's degree thesis, Kobe University, 1996.
20. N. Sotani, K. Eda, and M. Kunitomo, *J. Chem. Soc. Faraday Trans.* **86,** 1583 (1990).