  Bull. Chem. Soc. Jpn., 64, 161—164 (1991)

Formation of $Na_{0.9}Mo_6O_{17}$ in a Solid-Phase Process. Transformations of a Hydrated Sodium Molybdenum Bronze, $Na_{0.23}(H_2O)_{0.78}MoO_3$, with Heat Treatments in a Nitrogen Atmosphere

Kazuo EDA,* Kouichi FURUSAWA,† Fumikazu HATAYAMA,††
Sadao TAKAGI,† and Noriyuki SOTANI
College of Liberal Arts, Kobe University, Tsurukabuto,
Nada, Kobe 657
† Department of Chemistry, Faculty of Science and Technology,
Kinki University, Kowakae, Higashi-Osaka 577
†† School of Allied Medical Sciences, Kobe University,
Tomogaoka, Suma, Kobe 654-01
(Received August 22, 1990)

The transformations of hydrated sodium molybdenum bronze, $Na_{0.23}(H_2O)_{0.78}MoO_3$, with heat treatments in a nitrogen atmosphere are as follows: $Na_{0.23}(H_2O)_{0.78}MoO_3$ (AD) $\xrightarrow{\text{at 330 K}}$ $Na_{0.23}(H_2O)_{0.5}MoO_3$ (VD) $\xrightarrow{\text{at 457 K}}$ $Na_{0.23}MoO_3$ (with VD structure) $\xrightarrow{\text{at 583 K}}$ $Na_{0.9}Mo_6O_{17}$ + a small amount of other materials $\xrightarrow{\text{at 800 and 900 K}}$ melt. This indicates a new and variable formation process of alkali metal molybdenum bronzes. In this process, $Na_{0.9}Mo_6O_{17}$ was formed in the solid phase without the formation of any intermediate products. Its formation temperature was about 600 K, which was less than those of the usual preparation methods by about 200 K.

It is well-known that alkali metal molybdenum bronzes exhibit low-dimensional electronic properties.[1-3] They are semiconductors and most of them show a semiconductor-metal transition.[4-7] In particular, $Li_{0.9}Mo_6O_{17}$ is known to exhibit superconductivity.[8] They have been extensively studied because of interest in these properties.[1-11] On the other hand, hydrated alkali molybdenum bronzes, $A_x(H_2O)_yMoO_3$, have been synthesized by Schöllhorn et al.[12] These bronzes are apparently different regarding their Mo–O frameworks from the metal bronzes; i.e., hydrated bronzes possess a Mo–O framework based on the MoO_3 structure, while the metal bronzes possess different Mo–O frameworks.[13] However, their compositions are similar to each other, excluding the hydration water. We have thus been interested in the structural changes of hydrated molybdenum bronzes after removing the hydration water. We therefore investigated the structural changes of a hydrated sodium molybdenum bronze with heat treatments in a nitrogen atmosphere and found that $Na_{0.9}Mo_6O_{17}$ is formed from the hydrated bronze. Alkali metal molybdenum bronzes have usually been synthesized by an electrolytic reduction of A_2MoO_4–MoO_3 melts and by heating stoichiometric mixtures of A_2MoO_4, MoO_3, and MoO_2 in a vacuum.[1-11] In these syntheses, the formations of the bronzes proceed in a liquid phase above 800 K. The formation of $Na_{0.9}Mo_6O_{17}$ from a hydrated bronze proceeds at about 600 K in the solid phase without the formation of any intermediate products. This fact not only suggests that the formation proceeds by way of a new mechanism, but also provides a new and variable synthesis method of alkali metal molybdenum bronzes. This paper describes them in full detail.

Experimental Procedure and Results

Preparation. Hydrated sodium molybdenum bronze was prepared by Thomas and McCarron, III's method.[13] The composition of the hydrated bronze was $Na_{0.23}(H_2O)_{0.78}MoO_3$.

Differential Thermal Analysis. TG–DTA was carried out in a nitrogen atmosphere on a MAC SCIENCE TG–DTA 2000. A TG–DTA heating curve was obtained at a heating rate of 10 K min^{-1}, while a cooling curve was gotten by cooling naturally.

The TG–DTA curve of hydrated sodium molybdenum bronze is shown in Fig. 1. Four endothermic (at 330, 457, 800, and 927 K) and two exothermic peaks (at 583 and 633 K) can be seen. The endothermic peaks at 330 and 457 K are

Table 1. The Results of Analysis

Treatment condition	H_2O wt%[a]	Mo wt%	Na wt%	Mo^{5+}/total Mo
As-prepared	8.7	59.4 (65.1)	3.3 (3.6)	0.23
420 K	5.7	62.1 (65.9)	3.5 (3.7)	0.21
520 K	4.3[b]	62.2 (65.0)	3.5 (3.7)	0.21
600 K	0	65.8 (65.8)	3.5 (3.5)	0.22
650 K	0	64.8 (64.8)	3.6 (3.6)	0.23
840 K	0	64.8 (64.8)	3.6 (3.6)	0.22

a) This value is given by TG analysis. b) This value means the re-hydration water on cooling. Values in parentheses are calculated by excluding water contents.

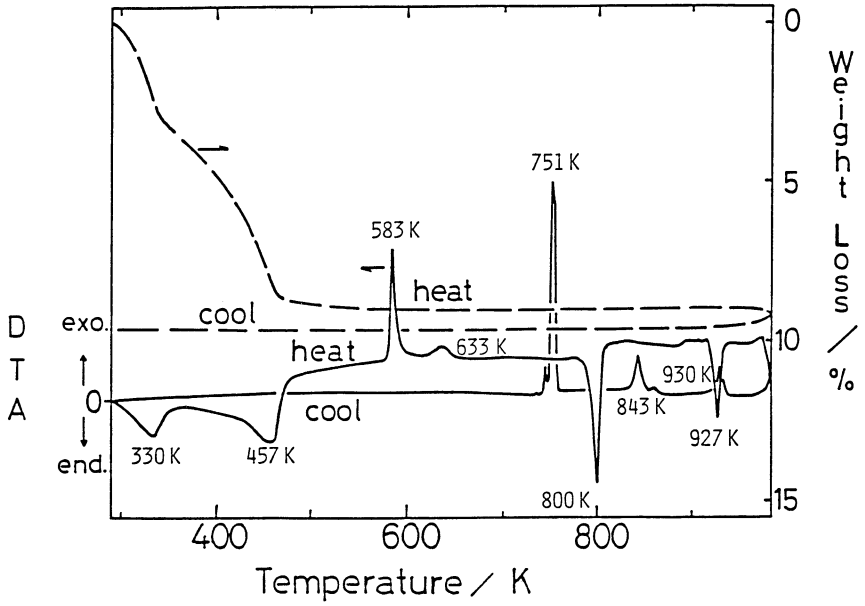

Fig. 1. TG–DTA curve of the hydrated sodium molybdenum bronze in a nitrogen atmosphere on heating and on cooling.

accompanied by a large weight loss, while the other peaks are not. The peaks at 330, 457, 583, and 633 K disappear upon cooling, and arise from irreversible phase transformations, while the peaks at 800 and 927 K are reversible transformations. The peaks at 330 and 457 K are attributed to the release of hydration water, due to the large weight losses.

Investigation of Phase Transformations. The samples heated both before and after each DTA peak temperature were investigated in detail using chemical analysis and an X-ray diffraction (XRD) method. Samples heated below 520 K were dark blue in color and those heated above 600 K were dark red. Sintering of the sample occurred above 800 K. The Na and Mo contents in the samples were measured by using a HITACHI 180-80 atomic absorption spectrophotometer with the 3302.3 Å line of Na and the 3132.6 Å line of Mo. The Mo^{5+} contents of the samples were determined chemically by Choain and Marion's method.[14] XRD patterns were obtained by using a RIGAKUDENKI GEIGER D-1 FLEX diffractometer with Cu $K\alpha$ radiation. Samples for the measurements were mixed with an internal standard (ca. 5 wt% Si).

The analytical results are summarized in Table 1. The quantity of Mo^{5+} remains constant. Upon heat treatments, as increase in the heating temperature, the H_2O content of the sample decreases. Samples heated below 520 K contain H_2O and those heated above 600 K do not. According to a differential thermal analysis, a sample after an endotherm at 457 K should contain no hydration water. Nevertheless, a sample heated at 520 K contains 4.3 wt% of water. When the sample was cooled to room temperature, the weight gain was observed by TG measurements. Therefore, the water in the sample is re-hydration water. The composition of a sample heated above 600 K is $Na_{0.23}MoO_3$, while that of a sample heated at 420 K is $Na_{0.23}(H_2O)_{0.5}MoO_3$. The real composition of a sample at 520 K is $Na_{0.23}MoO_3$. The XRD patterns of the samples are shown in Fig. 2. An as-prepared sample and a sample heated at 420 K are identical with an air-dried

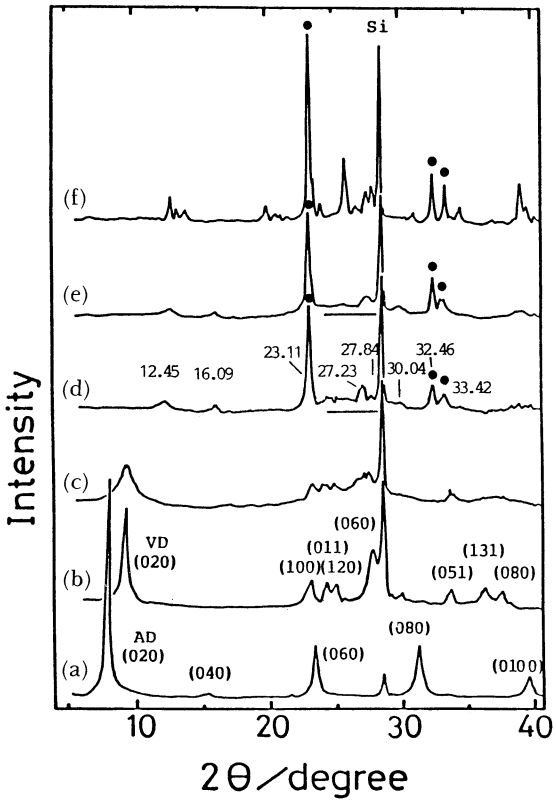

Fig. 2. Changes in X-ray diffraction patterns of the hydrated sodium molybdenum bronze by heat treatments in a nitrogen atmosphere. (a) as-prepared, and heated (b) at 420 K, (c) at 520 K, (d) at 600 K, (e) at 650 K, and (f) at 840 K.

hydrated sodium molybdenum bronze (denoted as AD), $[Na(H_2O)_x]_{0.25}MoO_3$ ($2<x\leqslant 6$), and an vacuum-dried hydrated sodium molybdenum bronze (denoted as VD), $[Na(H_2O)_2]_{0.25}MoO_3$, of Thomas and McCarron, III, respectively.[13] A sample heated at 520 K still maintains its VD structure, although the diffraction peaks become rather broad. By heating at 600 K, the diffraction peaks of VD disappear and new peaks appear at 12.45, 16.09, 23.11, 27.23, 27.84, 30.04, 32.46, and 33.42°. The peaks marked by the symbol ● are attributed to $Na_{0.9}Mo_6O_{17}$.[10] Others show the formation of a small amount of MoO_3 and $Na_2Mo_2O_7$. A sample heated at 650 K gives nearly the same diffraction pattern as that at 600 K, except for minor differences in the range 24—28°. For a sample heated at 840 K, the diffraction peaks of $Na_{0.9}Mo_6O_{17}$ remain, though many other peaks also appear. These peaks are attributed to MoO_3 and a solid solution of $Na_2Mo_4O_{13}$+ MoO_3.[15]

Discussion

Transformations in a Nitrogen Atmosphere. The first release of hydration water gives rise to a transformation from AD to VD. After the second release of hydration water, i.e., the complete removal of the hydration water, the sample still retains the VD structure up to 583 K. This sample can incorporate water molecules from the atmosphere. The broadening in the XRD pattern of this sample (Fig. 2(c)) may be due to inadequate hydration.[16] The main product of a sample heated at 600 K was $Na_{0.9}Mo_6O_{17}$. The DTA peak at 583 K is, therefore, attributed to a transformation from VD to $Na_{0.9}Mo_6O_{17}$. According to the X-ray results, though the sample before and after the DTA peak at 633 K give no characteristic change, a minor difference appears in the range 24—28°. A differential thermal analysis of the hydrated bronze with lower Na content[17] revealed that the peak at 633 K is also correlated to the formation of $Na_{0.9}Mo_6O_{17}$. The DTA endothermic peaks at 800 and 927 K are reversible. Appreciable sintering of the sample took place above 800 K, as mentioned above. Thus, these peaks are due to melting of the sample. Compared with the phase diagram of Na_2MoO_4 and MoO_3,[15] we presume that the peaks at 800 and 927 K arise from transformations to an equilibrium mixture of the solid and solution and to solution, respectively. According to chemical analyses, the compositions of the samples heated above 583 K are $Na_{0.23}MoO_3$. On the other hand, the composition of the dominant product is $Na_{0.9}Mo_6O_{17}$. The appearance of a few materials other than $Na_{0.9}Mo_6O_{17}$ in samples heated above 600 K may result from a deviation of the compositions of the samples from $Na_{0.9}Mo_6O_{17}$. Transformations of the hydrated bronze with heat treatments in a nitrogen atmosphere are formulated as follows:

$$\underset{(Na_{0.23}(H_2O)_{0.78}MoO_3)}{\text{AD}} \xrightarrow[\text{at 330 K}]{\text{end. peak}} \underset{(Na_{0.23}(H_2O)_{0.50}MoO_3)}{\text{VD}} \xrightarrow[\text{at 457 K}]{\text{end. peak}} \underset{(Na_{0.23}MoO_3^{\#})}{\text{VD structure}} \xrightarrow[\text{at 583 K}]{\text{exo. peak}} Na_{0.9}Mo_6O_{17} + \text{other} \xrightarrow[\text{at 633 K}]{\text{exo. peak}}$$

$$Na_{0.9}Mo_6O_{17} + \text{other}^{!} \xrightarrow[\text{at 800 K and 927 K}]{\text{end. peaks}} \text{melt}$$

#When cooled in the presence of water vapor, this sample with a VD structure can easily contain re-hydration water. !Other materials, which are identical with MoO_3 and $Na_2Mo_2O_7$, are contained in small amounts.

Formation Mechanism of $Na_{0.9}Mo_6O_{17}$. $Na_{0.9}Mo_6O_{17}$ was formed at 583 K from a hydrated sodium molybdenum bronze. The sample has a VD structure just before the formation of $Na_{0.9}Mo_6O_{17}$. The formation temperature is lower than the melting points of the sample by at least 200 K. These facts indicate that the formation proceeds directly from VD in the solid-phase process. This formation mechanism is different from those by usual methods. By the usual methods, the formation proceeds in the liquid phase and via intermediate products with similar structures.[7,10] The formation of $Na_{0.9}Mo_6O_{17}$ from VD is a structural phase transition. Formation at a lower temperature (based on the phase transition) may arise from the fact that the hydrated bronze possesses Na atoms already inserted in the Mo–O framework. The structures of $Na_{0.9}Mo_6O_{17}$ and VD have already been reported,[11,13] as shown in Fig. 3. These structures can be described as being slabs connected by Na atoms. The slab of $Na_{0.9}Mo_6O_{17}$ is build up of 4 layers of Mo octahedra and 2 layers of tetrahedra sharing corners, while that of VD contains 2 layers of Mo octahedra sharing edges. An inspection of these two structures suggests that the direct formation of $Na_{0.9}Mo_6O_{17}$ from VD is possible through the following steps, as shown in Fig. 3(b): (i) passing of Na atoms through the slabs, (ii) linkage of each two slabs, and (iii) reformation of the Mo–O framework. The radius of a sphere which can pass through an open space in the slabs of VD may be smaller than 0.3 Å. This value is obtained from well established atomic positions of $D_{0.36}MoO_3$,[18] of which the Mo–O framework is comparable to that of VD. (An ion radius of O atom, 1.4 Å, was used.[19]) The ion radius of Na atoms is 1.12 Å[20] and is too large to pass through the open space. However, the chemical bonds in the bronze are expected to be rather loose at 600 K, which corresponds to a few hundred degree below its melting point. The loose bonds may permit Na atoms to pass through the slabs.

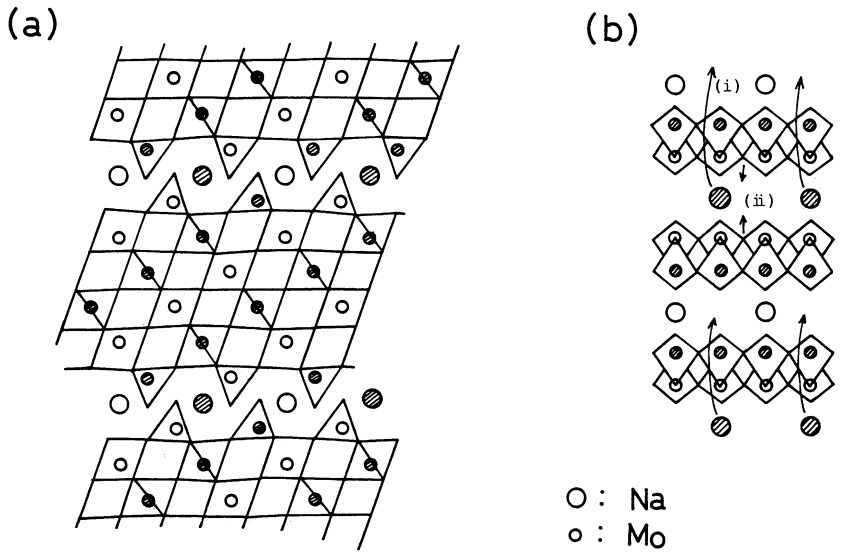

Fig. 3. Crystal structures of (a) $Na_{0.9}Mo_6O_{17}$ and (b) VD. Open and hatched circles indicate atomic positions at $Z=0$ and 1/2, respectively.

The formation of $Na_{0.9}Mo_6O_{17}$ from VD is a new formation process, which stimulates not only great interest in the physical phenomenon, but also merits for applications. The preparation of alkali metal molybdenum bronzes from hydrated alkali molybdenum bronzes can be performed at a lower temperature than by the usual fused methods. The preparation of bronzes in a thin film or a complex form is also possible, since the formation of bronzes proceeds in a solid-phase process without any formation of melts. In this work, the formation of $Na_{0.9}Mo_6O_{17}$ was accompanied by the coexistence of a small amount of other materials. This prevents a realization of the above applications. To prepare bronzes without such a coexistence, the composition of the hydrated sodium molybdenum bronze must be controlled. Methods to control the composition are now being studied. Moreover, an investigation regarding other hydrated alkali molybdenum bronzes is also in progress.

References

1) M. Greenblatt, *Chem. Rev.*, **88**, 31 (1988).
2) D. S. Perloff, M. Vlasse, and A. Wold, *J. Phys. Chem. Solids, Suppl.*, **1**, 361 (1967).
3) M. H. Whangbo and L. F. Schneemeyer, *Inorg. Chem.*, **25**, 2424 (1986).
4) A. Wold, W. Kunnmann, R. J. Arnott, and A. Fekrretti, *Inorg. Chem.*, **3**, 545 (1964).
5) A. Wold, *Bull. Soc. Chim. Fr.*, **1965**, 1059.
6) G. H. Bouchard, J. Perlstein, and M. J. Sienko, *Inorg. Chem.*, **6**, 1682 (1967).
7) P. Strobel and M. Greenblatt, *J. Solid State Chem.*, **36**, 331 (1981).
8) M. Greenblatt, W. H. McCarroll, R. Neifeld, M. Croft, and J. V. Waszczak, *Solid State Commun.*, **51**, 671 (1984).
9) J. M. Reau, C. Fouassier, C. Gleitzer, and M. Parmentier, *Bull. Soc. Chim. Fr.*, **1970**, 479.
10) K. V. Ramanujachary, M. Greenblatt, and W. H. McCarroll, *J. Cryst. Growth*, **70**, 476 (1984).
11) B. M. Gatehouse, D. J. Lloyd, and B. K. Miskin, "Solid State Chemistry," NBS Special Publication 364, ed by R. S. Roth and S. J. Schneider, V. S. Dept. of Commerce, Washington, D. C.(1972), p. 15.
12) R. Schöllhorn, R. Kuhlmann, and J. O. Besenhard, *Mater. Res. Bull.*, **11**, 83 (1976).
13) D. M. Thomas and E. M. McCarron, III, *Mater. Res. Bull.*, **21**, 945 (1986).
14) C. Choain and F. Marion, *Bull. Soc. Chim. Fr.*, **1963**, 212.
15) P. Caillet, *Bull. Soc. Chim. Fr.*, **1967**, 4750.
16) Sodium atoms in original VD are octahedrally coordinated by two oxygen atoms of hydration water molecules and four terminal oxygen atoms of MoO_3.[13] However, some of sodium atoms in this sample are not octahedrally coordinated, because of the lack of hydration water. This generates distortions of the lattice and gives rises to the broadening.
17) Thermal differential analysis was carried out for the hydrated sodium bronze of which Na content was reduced by a treatment with an acidic solution, i.e., Na^+–H^+ ion-exchange. As Na content decreased, the exothermic peak at 583 K shifted to a higher temperature side and finally overlapped with the peak at 633 K. For the bronze with Na/Mo=0.16, which showed only one exothermic peak at 633 K, $Na_{0.9}Mo_6O_{17}$ was formed at the peak temperature.
18) P. G. Dickens, J. J. Birtill, and C. J. Wright, *J. Solid State Chem.*, **28**, 185 (1979).
19) R. B. Heslop and K. Jones, "Inorganic Chemistry," Elsevier Scientific Publishing Co., Amsterdam (1976).
20) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th Edition, John Wiley & Sons, New York (1988).