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Structural and Compositional Changes of Hydrated Sodium Molybdenum Bronze by Heat Treatments in Air

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Synopsis. When hydrated sodium molybdenum bronze, VD, was heated in air, dehydration as well as both irreversible and reversible phase changes took place as follows:

$$Na_{0.22}(H_2O)_{0.43}H_{0.03}MoO_{3.11} \xrightarrow{442\ K} Na_{0.21}H_{0.03}MoO_{3.14}$$
$$\xrightarrow{555\ K} Na_2Mo_4O_{13} + MoO_3 \xrightarrow{801\ K} \text{melt.}$$

Interest has been focused on studies of alkali molybdenum bronzes which show low-dimensional electronic properties,[1] such as semiconductor-metal transitions[2,3] and superconductivity.[4] Wold et al.[2] first prepared sodium molybdenum bronze, $Na_{0.9}Mo_6O_{17}$, by fusing the desired molar proportion of a mixture of MoO_3 and Na_2MoO_4 at 823 K for 1 h. However, the authors[5] obtained $Na_{0.9}Mo_6O_{17}$ from the hydrated sodium molybdenum bronze by heating in nitrogen at about 600 K. This is a useful and effective preparation method for the following reasons: (1) The treating temperature is lower by about 200 K than that for the usual fused method. (2) Although the usual preparation method of $Na_{0.9}Mo_6O_{17}$ proceeds in the liquid phase, in our method there is a solid phase without any intermediate products.[5] (3) The hydrated sodium molybdenum bronze already contains Na before any treatment. It is, therefore, important to have detailed information concerning the hydrated sodium molybdenum bronze as a starting material for the preparation of $Na_{0.9}Mo_6O_{17}$. However, no detailed characterization has yet been performed.[6–9] The authors have recently reported[10] on the characterization of hydrated sodium molybdenum bronzes by the use of TG-DTA and NMR. In a series of investigations concerning the hydrated alkali metal molybdenum bronze, we studied both the structural and compositional changes of the hydrated sodium molybdenum bronze by a heat treatment in air; they are described in this paper.

Experimental

The sample was obtained by the method of Thomas and MacCarron.[9] The air-dried sample (named "AD") was unstable. A sample called "VD" was stable and was used for the experiment; it was obtained from AD by vacuum drying at room temperature overnight or by standing in air for more than 30 d. TG-DTA curves were obtained using a MAC SCIENCE TG-DTA 2000 with a heating rate of 10 K min^{-1}. Samples heated at various temperatures were studied using a RIGAKUDENKI GEIGER D-1 FLEX X-ray diffractometer and a JASCO 701G IR spectrophotometer. Changes in surface area were measured using a QUANTACHROME QUNTASORB Jr. The contents of Na and Mo in the samples were measured using a HITACHI 180-80 atomic absorption spectrometer with the 330.23-nm line for Na and the 313.26-nm line for Mo. Mo^{5+} was determined by using the method of Choain and Marion.[11]

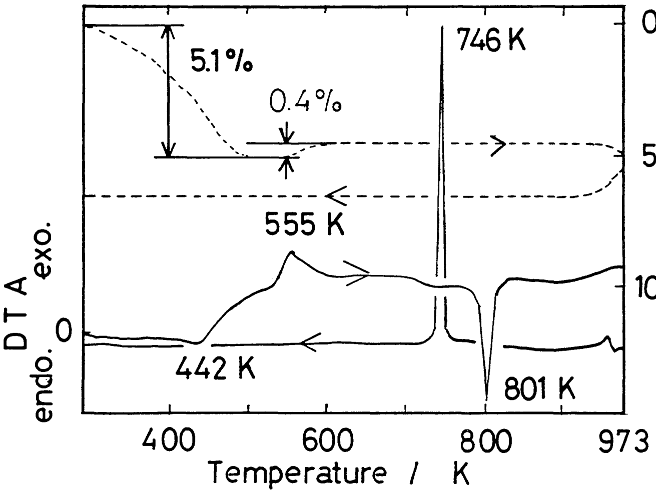

Fig. 1. TG-DTA curves of VD in air. The curves were obtained by heating (—>—) with a heating rate of 10 K min^{-1} and then by cooling (—<—) naturally to room temperature.

Results

Figure 1 shows the TG-DTA curves of hydrated sodium molybdenum bronze, VD, which were obtained by heating to 973 K and then cooling naturally to room temperature. Upon heating, two endothermic peaks at 442 and 801 K and an exothermic peak at 555 K appeared. The endothermic peak at 442 K was accompanied by a weight loss (5.1%) and the exothermic peak at 555 K, by a weight gain (0.4%); the endothermic peak at 801 K showed no weight change. Upon cooling, two exothermic peaks with no weight change appeared at 746 and 937 K. The endothermic peak at 442 K and the exothermic peak at 555 K upon heating gave no corresponding peak upon cooling. It is, therefore, suggested that an irreversible phase transition takes place. On the other hand, the endothermic peak at 801 K upon heating corresponds to the exothermic peak at 746 K upon cooling, and is attributed to a reversible phase transition.

Figure 2 shows the X-ray diffraction patterns of samples heated at various temperatures. The pattern of the sample heated at 498 K is identical with that of VD, although the X-ray peaks are broad. The samples heated at 593 and 828 K show patterns attributed to $Na_2Mo_4O_{13}$ and MoO_3.

The IR spectra of the samples heated at the same temperatures as in the case of X-ray studies were obtained. Although the spectra of samples heated at 423 and 498 K were identical with that of VD, those of the samples heated at 593 and 828 K were very complicated.

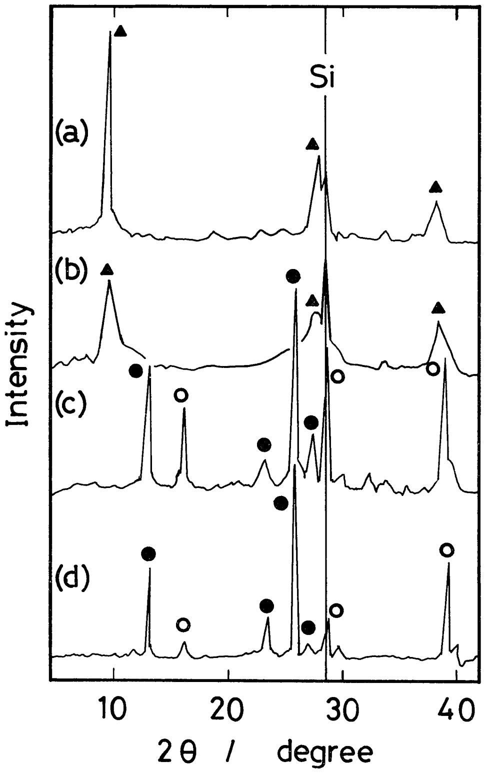

Fig. 2. X-Ray diffraction patterns of the samples heated in air at (a): 423, (b): 498, (c): 593, and (d): 828 K. ▲ represents VD, ●, MoO_3 and ○, $Na_2Mo_4O_{13}$, respectively.

The surface areas of the samples heated at the same temperatures as in the case of the X-ray studies are shown in Table 1. Although the surface areas of samples with the VD structure were nearly constant, they decreased steeply when samples with the VD structure were completely transformed to $Na_2Mo_4O_{13}$ and MoO_3. It is clear that the change in the surface area depends on the crystal structure.

The TG results and the results obtained by chemical analyses are given in Table 1. According to these results, samples having the VD structure necessarily contain Mo^{5+}, which is produced by reduction of Mo^{6+}, resulting from an insertion of cations. On the contrary, samples without the VD structure did not contain Mo^{5+}, even though they contained Na.

Discussion

According to chemical analyses, VD contains 0.25 mol of Mo^{5+} and 0.22 mol of Na^+, as shown in Table 1. The NMR results[10] have proved that VD contains protons. Considering these results, it is suggested that the concentration of protons is 0.03 (=0.25−0.22) mol. VD is therefore, formulated as $Na_{0.22}(H_2O)_{0.43}H_{0.03}MoO_{3.11}$. The weight gain (0.4%) at around 555 K should be due to a recombination of oxygens in air to make up for the lattice oxygens consumed by the protons. This value corresponds to 0.02 mol of oxygens and to 0.04 mol of protons, which agrees rather well with that of 0.03 mol evaluated from the results of the chemical analysis.

The results obtained by chemical analyses of the samples heated at 498 and 593 K are the same, except that a sample heated at 498 K contains 0.04 mol of Mo^{5+}. This sample has the VD structure. The NMR result also shows the presence of a small number of protons. Protons in a Type-I hydrogen bronze can be kept at a temperature of more than 550 K.[12] Considering these results, 0.03 mol of protons should be maintained in the

Table 1. Composition of Hydrated Sodium Molybdenum Bronze Heated at Various Temperatures in Air

	H_2O	Mo	Na	O	x	SA
	%	%	%	%	(Mo^{5+})	$m^2\ g^{-1}$
V D	5.10	60.36	3.33	31.21		10.1
a)	(0.43)	(1.00)	(0.22)	(3.11)	0.25	
423 K	3.29	61.90	3.11	31.69		9.1
a)	(0.28)	(1.00)	(0.21)	(3.07)	0.19	
498 K		64.50	3.30	32.20		8.8
a)		(1.00)	(0.21)	(3.14)	0.04	
593 K		63.48	3.22	33.30		3.5
a)		(1.00)	(0.21)	(3.14)	0.00	
733 K		64.20	3.40	32.40		1.6
a)		(1.00)	(0.22)	(3.03)	0.00	
828 K		63.56	3.28	33.16		0.3
a)		(1.00)	(0.22)	(3.13)	0.00	

a) Molar ratio to Mo.

sample. Therefore, the composition is $Na_{0.21}H_{0.03}MoO_{3.14}$; the sample heated at 593 K has a different structure, and the composition is $Na_{0.21}MoO_{3.14}$. This X-ray result proves that the sample heated at 593 K and then cooled to the room temperature comprises a mixture of $Na_2Mo_4O_{13}$ and MoO_3. The Na_2MoO_4/MoO_3 ratio of the sample is about 1/9, agreeing well with the range of coexistence with $Na_2Mo_4O_{13}$ and MoO_3 according to a Na_2MoO_4–MoO_3 phase diagram.[13-15] The exothermic peak at 555 K is due to an irreversible phase transition from VD to $Na_2Mo_4O_{13}$ and MoO_3.

The sample heated at 828 K and then cooled to room temperature apparently shows a glassy state. The X-ray results prove that it comprises $Na_2Mo_4O_{13}$ and MoO_3. According to the phase diagram, an eutectic temperature of 810 K appears when the $Na_2Mo_4O_{13}/MoO_3$ ratio is between 23/77 and 6/94. In this range, the samples can produce solid solutions at an eutectic temperature such as for $Na_2Mo_4O_{13}\cdot MoO_3$ and $Na_2Mo_4O_{13}\cdot 2MoO_3$.[13] Since the Na_2MoO_4/MoO_3 ratio of 1/9 found in this study just falls within this range and the X-ray results show the presence of $Na_2Mo_4O_{13}$ and MoO_3 (as mentioned above), it can be concluded that the endothermic peak at 801 K upon heating is due to the eutectic point, (which corresponds to the melting point of the solid solution), and the exothermic peak at 746 K upon cooling, to solidification. According to above consideration, we conclude that the hydrated sodium molybdenum bronze, VD, is changed by a heat treatment in air as follows:

$$Na_{0.22}(H_2O)_{0.43}H_{0.03}MoO_{3.11} \xrightarrow{442\text{ K}} Na_{0.21}H_{0.03}MoO_{3.14}$$
$$\xrightarrow{555\text{ K}} Na_2Mo_4O_{13} + MoO_3 \xrightarrow{801\text{ K}} \text{melt.}$$

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