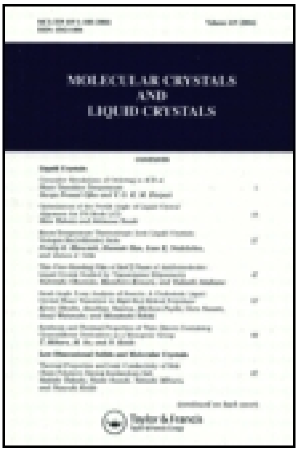

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The Possibility in the Formation of Alkali Molybdenum Bronzes from Hydrated Alkali Molybdenum Bronzes

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THE POSSIBILITY IN THE FORMATION OF ALKALI MOLYBDENUM BRONZES FROM HYDRATED ALKALI MOLYBDENUM BRONZES

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Abstract We will introduce a new synthesis method for alkali molybdenum bronzes. By this method the formation of the bronzes can proceed in solid phase and the formation temperature can be lowered than those by hitherto methods. Applications of the new method will be proposed.

INTRODUCTION

Alkali molybdenum bronzes, named alkali bronzes for convenience, are well-known to be interesting materials with low-dimensional electronic properties. Most of them give a semiconductor-metal transition.[1,2] Especially, $Li_{0.9}Mo_6O_{17}$ exhibits superconductivity, although it do at a very low temperature.[3] Due to interest in these properties, a lot of studies have been carried out on the bronzes. Up to now, three types of alkali bronzes, (1) red bronzes $A_{0.33}MoO_3$ (A: alkali metal), (2) blue bronzes $A_{0.30}MoO_3$, and (3) purple bronzes $A_{0.9}Mo_6O_{17}$, have been confirmed as the bronzes obtained at atmospheric pressure.[4] On the other hand, recently Mumme and Watts[5] and Canadell and Whangbo[6] have suggested existence of a new type of alkali bronze.

Syntheses of alkali bronzes have been achieved by a few methods. The methods and their characteristics are summarized below;

1) Heating a stoichiometric mixture of A_2MoO_4, MoO_3, and MoO_2.[7] By this method no alkali bronze single crystals are obtained.
2) Electrolytic reduction of A_2MoO_4-MoO_3 melts. Small single crystals are obtained on electrodes.[8]

3) Heating an appropriate mixture of A_2MoO_4, MoO_3, and MoO_2 with temperature gradient (Temperature Gradient Flux Technique).[9] Fairly large single crystals are obtained, although this method needs removal of extraneous products.

All these methods achieve the preparation at higher temperatures

temperature gradient (Temperature Gradient Flux Technique). Fairly
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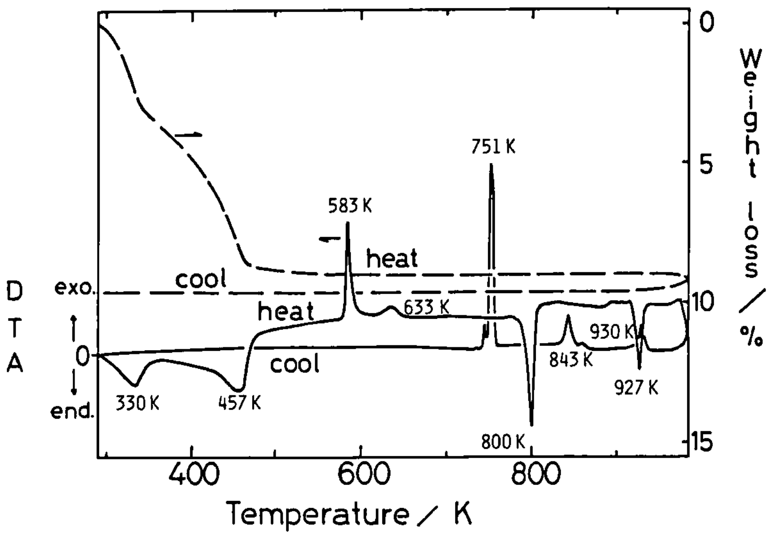

FIGURE 1. TG-DTA curve of the as-prepared sample in nitrogen atmosphere.

change, and two exothermic peaks at 583 and 633 K with no weight change on heating. The peaks at 330, 457, 583, and 633 K are irreversible. On the other hand, the peaks at 800 and 927 K are reversible.

The samples heated before and after each DTA peak temperature have been investigated. The color of the sample heated below 583 K was dark blue and the color of the sample heated at more than 583 K was dark red. It was recognized that appreciable sintering of the sample occurred when the sample was heated at a higher temperature than 800 K. Analytical results of the samples are shown in Table I. The quantity of Mo^{5+} does not vary and, of course, suggests that oxidation has never occurred. Furthermore, the results show that the compositions of all heated samples at higher temperatures than 583 K are $Na_{0.23}MoO_3$.

The X-ray diffraction patterns of the samples are shown in Fig. 2. According to the diffraction patterns, the sample as-prepared and heated at 420 K are identical with AD and VD hydrated sodium molybdenum bronze, respectively, which have been classified by Thomas and McCarron, III.[12] VD structure remains in the sample heated at 520 K. By heating at 600 K, the diffraction peaks of VD disappear and new diffraction peaks appear

TABLE I. The results of chemical analysis.

Treatment condition	Mo wt%	Na wt%	Mo^{5+} / total Mo
non-treatment	59.4 (65.1)	3.3 (3.6)	0.23
420K	62.1 (65.9)	3.5 (3.7)	0.21
520K	62.2 (65.0)	3.5 (3.7)	0.21
600K	65.8 (65.8)	3.5 (3.5)	0.22
650K	64.8 (64.8)	3.6 (3.6)	0.23
840K	64.8 (64.8)	3.6 (3.6)	0.22

A value in parentheses is calculated by excluding hydrate-water.

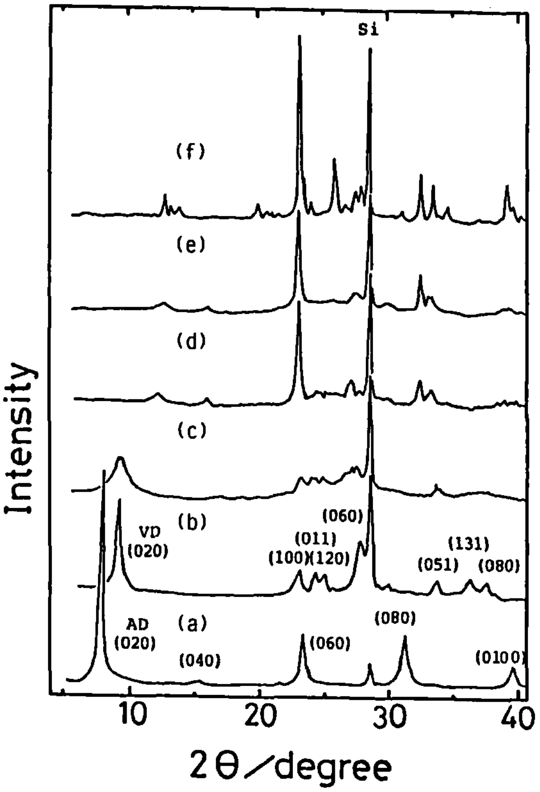

FIGURE 2. Changes in X-ray diffraction patterns of the hydrated sodium molybdenum bronze by heat-treatments in nitrogen atmosphere. (a) non-treatment, (b) at 420 K, (c) at 520 K, (d) at 600 K, (e) at 650 K, and (f) at 840 K.

at 12.45, 16.09, 23.11, 27.23, 30.04, 32.46, and 33.42°. The peaks are identified with those of $Na_{0.9}Mo_6O_{17}$ except for weak ones at 12.45 and 30.04°. For the sample heated at 650 K, minor differences in the range 24-28° of the diffraction pattern from that of the sample heated at 600 K is observed. For the sample heated at 840 K, a lot of other new peaks appear and indicate the formation of other material.

The endothermic peaks at 330 and 457 K with large weight loss have been attributed to release of hydrate-water. Our interest has been in the structure of the sample after the release of these hydrate-water. The exothermic peaks at 583 and 633 K have been attributed to the transformation from VD to $Na_{0.9}Mo_6O_{17}$ and to a minor rearrangement of the structure, respectively. On the other hand, reversible peaks at 800 and 927 K have been attributed to melting of the contents in the sample. The formation of other material with heating at 840 K may result from the deviation in composition of the sample ($Na_{0.23}MoO_3$) from $Na_{0.9}Mo_6O_{17}$.

This study shows that the formation of an alkali bronze from a hydrated bronze can be achieved even by a simple heat-treatment at nitrogen atmosphere.

EXPECTATION OF THE NEW PREPARATION METHOD

The above study shows not only substantiation of the preparation of alkali bronzes from hydrated bronzes, but also following merits in preparing alkali bronzes. The formation of $Na_{0.9}Mo_6O_{17}$ by using Fused Method need the heating temperature more than 800 K. However, by using the hydrated bronze as the starting material, the formation temperature can be lowered by about 200 K. And the formation temperature is much lower than melting points of reaction phase and it can be mentioned that the formation proceeds in solid phase. This may enable direct preparations of alkali bronzes in a thin film or in a complicated form. By using large hydrated bronze single crystals it may become feasible to prepare large alkali bronze single crystals. Preparations of the hydrated bronze single crystals have been already attempted by Schöllhorn et al.[10]

On the other hand, as mentioned above, it is easy to control alkali content in preparing hydrated bronzes. (Control range is restricted in

$0<x\leq 0.25$, x: alkali content.) And the new method may prepare alkali bronzes without any formation of liquid phase. These may enable the independent alkali content control of liquid phase which is mentioned in introduction and the preparation from the appropriately controlled hydrated bronzes may give new types of alkali bronzes.

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