Low-temperature Synthesis Routes of Alkali-metal Molybdenum Bronzes

Kazuo Eda,* Kin Chin, and M. Stanley Whittingham†
Department of Chemistry, Faculty of Science, Kobe University, Nada-ku, Kobe 657-8501
†*Institute for Materials Research, State University of New York at Binghamton, Binghamton, NY 13902-6000, U.S.A.*

(Received May 17, 1999; CL-990389)

We found some novel synthesis routes for alkali-metal molybdenum bronzes. The synthesis techniques are composed of simple hydrothermal treatments of mixed-valence compounds (or mixtures) with ACl or ACl+AOH aqueous solutions (A=alkali metal). Using these routes blue bronze ($K_{0.30}MoO_3$) and red bronze ($K_{0.33}MoO_3$) were obtained from hydrogen molybdenum bronze H_xMoO_3 or H_xMoO_3 + MoO_3 even at 410 K.

Alkali-metal molybdenum bronzes are mixed-valent ternary oxides, which exhibit interesting properties, such as low-dimensional electronic conductivity. Many studies have been performed on them.[1-9] These bronzes have been prepared from A (alkali metal)-Mo-O mixtures by several methods: 1) by electrolytic reduction of molten mixtures of A_2MoO_4-MoO_3, 2) by heat-treatments of mixtures such as A_2MoO_4-MoO_3-MoO_2 in sealed tubes, and so on.[1,2] These preparations are, generally, carried out at temperatures exceeding 800 K. In this decade, the Manthiram group[10,11] and we[12-15] have independently proposed new synthesis routes, in which non-stoichiometric single-phase compounds (amorphous compounds for the Manthiram group and intercalation compounds for us) are used as starting materials of the syntheses. In these routes the bronzes are formed at lower temperatures, around 600 K, some 200-300 K below those used in the ordinary methods, and a novel phase, which has never been prepared by usual synthesis techniques, has been obtained.[15] It is of great interest to solid state chemists in recent years to develop new synthesis routes that can bring down the synthesis temperatures and/or can provide novel compounds.

Recently we have found out that selective extraction of specific species by a leaching technique, based on the differences in solubility, gives interesting synthesis routes for mixed-valence compounds.[16] Then, hydrothermal techniques have been known to be very powerful methods which can lower synthesis temperatures and allow formation of novel compounds, never prepared by traditional high-temperature syntheses.[17-23] We have tried to combine both techniques to make further developments. In this work we found that alkali-metal molybdenum bronzes were formed at much lower temperature (lower than 473 K). These findings afford very useful synthesis routes for alkali-metal molybdenum bronzes and are expected to be applied to syntheses of other materials. So we will present the findings briefly.

In the present work hydrothermal treatments of H_xMoO_3, which is a hydrogen insertion compound of layered molybdenum trioxide and can be prepared from MoO_3 at ambient temperature,[24,25] or a mixture of H_xMoO_3 and MoO_3 with various x values with ACl or ACl+AOH aqueous solution were tested at various temperatures in the range 373-473 K. H_xMoO_3's with various x values were prepared by the chemical reduction of MoO_3, as reported previously.[25] The hydrothermal treatment was performed using a NICHIDENRIKA GLASS MAC-2 mini autoclave (a Teflon-lined stainless steal reactor) with 60 ml of volume. 30 ml of the solution and ca. 1.3 g of the starting solid (H_xMoO_3 or H_xMoO_3+MoO_3), which would give 0.3 M of solution, if soluble in the solution, were used for the treatment. After the treatment the products were filtrated, washed well with water, and investigated by X-ray diffraction (XRD), chemical and atomic absorption analyses, scanning electron microscopy (SEM), and so on.

We found that potassium metal molybdenum bronzes were formed even at 410 K by the treatments. Figure 1 shows the XRD patterns of the products obtained by the treatments of H_xMoO_3 or the mixture, with various x (initial x) values, with KCl aqueous solution at 430 K for 3 days ([KCl]= 0.6 M). According to the patterns the products for initial x=0.25, 0.30, and 0.70 consist of blue bronze ($K_{0.30}MoO_3$) + MoO_3, red bronze ($K_{0.33}MoO_3$) + MoO_3, and red bronze + MoO_2, respectively (Figures 1a, b, and d). The product for an initial x=0.50 is almost a single-phase of red bronze, but contains very small portions of MoO_3 and MoO_2 (Figure 1c). In the present work we used various kinds of combinations to prepare the starting solid with a certain initial x, for example, 42% $H_{0.71}MoO_3$ + 58% MoO_3, 87% $H_{0.26}MoO_3$ + 13% $H_{0.56}MoO_3$, and so on for the case of initial x=0.30. The products did not depend on the kinds of combinations, except for the cases leading to blue bronze (for initial x=0.25). The pattern

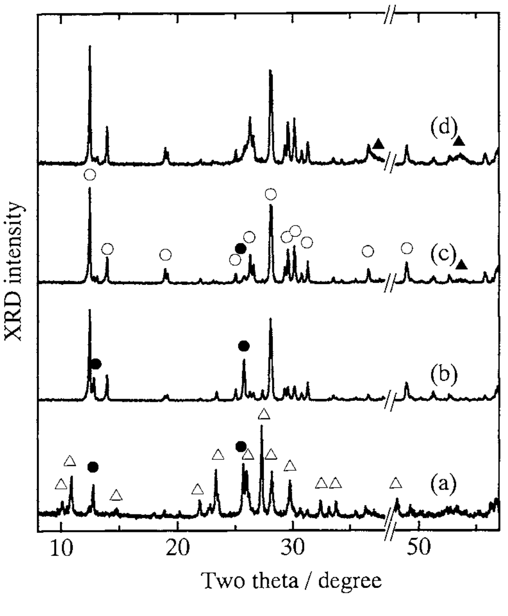

Figure 1. XRD patterns of the products obtained by the treatments of the starting solids with various x values with 0.6 M KCl solution at 430 K for 3 days: (a) x=0.25, (b) 0.3, (c) 0.5, and (d) 0.7. △, ○, ●, and ▲ indicate blue bronze, red bronze, MoO_3, and MoO_2, respectively.

Table 1. Treatments conditions and obtained products

Treatments			Products		
Solution		Solid			
KCl / M	*KOH* / M	*O.No.Mo*^{a}	*O.No.Mo*^{a}	*K/Mo*^{b}	*Yield* / g
0.6	0.0	5.75	5.84	0.21	1.1
0.6	0.0	5.70	5.79	0.34	1.1
0.6	0.0	5.50	5.61	0.36	1.1
0.6	0.0	5.30	5.30	0.32	1.2
0.6	0.08	5.75	5.73	0.44	1.1
0.6	0.30	5.75	5.21	0.34	0.4
0.6	0.45	5.75	4.63	0.21	0.2

^{a} The average oxidation number of Mo. ^{b} Molar ratio.

of Figure 1a, which indicates the formation of blue bronze, is for the product obtained from a single phase of $H_{0.25}MoO_3$. The products from the mixtures with initial x=0.25, such as 22% $H_{1.15}MoO_3$ + 78% MoO_3, gave the patterns of red bronze + MoO_3. The results of atomic and chemical analyses for the products, shown in Figure 1, are given in Table 1 (upper half). According to the results, the average oxidation number of Mo in solid increases after the hydrothermal treatments. This seems to result from oxidation of the material by air in the autoclave during the treatment. We have confirmed that the oxidation can be avoided by substitution N_2 for the air. Moreover, the results in the oxidation number of Mo and K contents support that the product for initial x=around 0.5 will be a single phase of red bronze (O.No.Mo=5.67 and K/Mo=0.33, see Table 1). The simultaneous formation of MoO_3 and MoO_2, observed as very minor portions for the product of an initial x=0.5, seems to result from heterogeneous reactions during the treatment in the condition where we could not perform constant stirring. The heterogeneous reactions will be avoided by performing the stirring. According to the SEM investigation on the products, the obtained red bronze was composed of needle-shaped crystallites with a size of ca. 1 x 1 x 10 μm^3. As for the blue bronze we have not found yet any proper condition to get it as a single phase, although we have tested various conditions. We will determine the specific condition in future.

Furthermore, it was also confirmed that we could obtain the products with higher reduction degree (ie., smaller oxidation number of Mo) than that of the starting solid by the hydrothermal treatment with KCl+KOH aqueous solutions, without using any reducing reagent. In Table 1 (lower half) the results are also given of atomic and chemical analyses for the products obtained by hydrothermal treatments of $H_{0.25}MoO_3$ with KCl+KOH aqueous solutions at 430 K for 3 days ([KCl]= 0.6 M and various KOH concentrations). The average oxidation number of Mo of product decreases as the KOH concentration in the treating solution becomes higher. This may result from the selective extraction of Mo^{6+} species by the alkaline solution, as mentioned previously.[16] According to the XRD investigation the products, obtained by the treatments with ACl+AOH, consisted mainly of red bronze and/or MoO_2.

The above findings indicate that the treatments in the present work will be some effective synthesis routes of alkali-metal molybdenum bronzes, which allow the very lower synthesis temperature than ordinary ones and control in the reduction degree of the products without using any reducing reagent. The routes can also be applied to the syntheses of other mixed-valence compounds.

References

1 A. Manthiram and J. Gopalakrishnan, *Rev. Inorg. Chem.*, **6**, 1 (1984).
2 M. Greenblatt, *Chem. Rev.*, **88**, 31 (1988).
3 M.-H. Whangbo, M. Evain, E. Canadell, and M. Ganne, *Inorg. Chem.*, **28**, 267 (1989).
4 K. Breuer, K.E. Smith, M. Greenblatt, W. McCarroll, and S.L. Hulbert, *J. Phys. Chem. Solids*, **57**, 1803 (1996).
5 M.E. Itkis, B.M. Emerling, and J.W. Brill, *Phys. Rev. B: Condens. Matter*, **56**, 6506 (1997).
6 L.-C. Duda, J.H. Guo, J. Nordgren, C.B. Stagarescu, K.E. Smith, W. McCarroll, K. Ramanujachary, and M. Greenblatt, *Phys. Rev. B: Condens. Matter*, **56**, 1284 (1997).
7 H. Requardt, R. Currat, P. Monceau, J.E. Lorenzo, A.J. Dianoux, J.C. Lasjaunias, and J. Marcus, *J. Phys.: Condens. Matter*, **9**, 8639 (1997).
8 M. Qjani, A. Arbaoui, A. Ayadi, and J. Dumas, *Ann. Chim.*, **23**, 237 (1998).
9 G. Grüner, *Physica B*, **244**, 70 (1998).
10 C. Tsang, A. Dananjay, J. Kim, and A. Manthiram, *Inorg. Chem.*, **35**, 504 (1996).
11 C.F. Tsang and A. Manthiram, *J. Mater. Chem.* **7**, 1003 (1997).
12 K. Eda, K. Furusawa, F. Hatayama, S. Takagi, and N, Sotani, *Bull. Chem. Soc. Jpn.*, **64**, 161 (1991).
13 N. Sotani, K. Eda, M. Yanagi-ishi, and S. Takagi, *Mater. Res. Bull.*, **28**, 363 (1993).
14 N. Sotani, T. Miyazaki, K. Eda, and F. Hatayama, *J. Mater. Chem.* **7**, 2253 (1997).
15 K. Eda, T. Miyazaki, F. Hatayama, and N. Sotani, *J. Solid State Chem.*, **137**, 12 (1998).
16 K. Eda, N. Matsuura, and N. Sotani, *Chem. Lett.*, **1997**, 1047.
17 M.S. Whittingham, *Curr. Opin. Solid State Mater. Sci.*, **1**, 227 (1996).
18 M.E. Davis and I.E. Maxwell, *Curr. Opin. Solid State Mater. Sci.*, **1**, 55 (1996).
19 J.R. Günter, M. Amberg, and H. Schmalle, *Mater. Res. Bull.*, **24**, 289 (1989).
20 K.P. Reis, A. Ramanan, and M.S. Whittingham, *J. Solid State Chem.*, **96**, 31 (1992).
21 T.G. Chirayil, E.A. Boylan, M. Mamak, P.Y. Zavalij, and M.S. Whittingham, *Chem. Commun.*, **1997**, 33.
22 Y. Oka, T. Yao, N. Yamamoto, and O. Tamada, *Mater. Res. Bull.*, **32**, 59 (1997).
23 R. Chen, P.Y. Zavalij, M.S. Whittingham, J.E. Greedan, N.P. Raju, and M. Bieringer, *J. Mater. Chem.*, **9**, 93 (1999).
24 J.J. Birtill and Dickens, *Mater. Res. Bull.*, **13**, 311 (1978).
25 N. Sotani, K. Eda, M. Sadamatsu, and S. Takagi, *Bull. Chem. Soc. Jpn.*, **62**, 903 (1987).