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Hydrothermal synthesis of potassium molybdenum oxide bronzes: structure-inheriting solid-state route to blue bronze and dissolution/deposition route to red bronze

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Abstract

The hydrothermal syntheses of the alkali metal molybdenum bronzes from starting solids (H_xMoO_3) with structural affinities to the desired products were investigated. Single-phase potassium blue and red bronzes were prepared by the hydrothermal treatments at around 430 K, and characterized by powder X-ray diffraction, IR spectroscopy, and SEM. The formation processes of these two bronzes during the hydrothermal treatments were found to differ. The blue bronze was formed by a structure-inheriting solid-state route from H_xMoO_3 with $x<0.3$, whereas the red bronze was formed for $x>0.3$ through a solution dissolution/deposition route via the formation of MoO_3+MoO_2.

Keywords: Low-temperature synthesis; Hydrothermal synthesis; Potassium metal molybdenum bronze; Formation mechanism

1. Introduction

The following three types of alkali metal molybdenum bronzes are well known: (i) blue bronze, $A_{0.3}MoO_3$ with $A =$ K, Rb, Tl, and Cs [1,2]; (ii) red bronze, $A_{0.33}MoO_3$ with $A =$ Li, K, Rb, Cs, and Tl [3]; and (iii) purple bronze, $A_{0.9}Mo_6O_{17}$ with $A =$ Li, Na, K and Tl [4,5]. The structures of the blue and red bronzes have similar sheet structures consisting of clusters of ten edge-sharing MoO_6 octahedra and six edge-sharing MoO_6 octaheda, respectively, while the structure of the purple bronze consists of ReO_3-type slabs of corner-shared MoO_6 octahedra, having MoO_4 tetrahedra at the surfaces of these slabs, as shown in Fig. 1. The physical properties of the blue and purple bronzes have been extensively studied because of their charge density wave phenomenon arising from their low-dimensional metallic character [6,7]. For example blue $K_{0.30}MoO_3$ and purple $K_{0.9}Mo_6O_{17}$ show Peierls transitions at ca. 180 and 120 K, respectively. Recently, the Zawilski group reported the possible existence of a CDW in red $K_{0.33}MoO_3$ below the Peierls transition temperature of 450 K [8].

Traditionally, the alkali metal bronzes have been prepared mainly by molten salt methods at temperatures exceeding 800 K: (i) electrolytic reduction of molten mixtures of MoO_3 and A_2MoO_4, and (ii) reaction of stoichiometric mixtures of A_2MoO_4, MoO_3 and MoO_2 [7,9]. More recently some low-temperature syntheses of the bronzes have been reported [10–15].

Recently, we have focused our work on hydrothermal synthesis of alkali metal molybdenum bronzes from solids (H_xMoO_3, which is a hydrogen-insertion compound of layered MoO_3) with structural affinities to the target products [16–18]. In the present work, we could obtain single-phase potassium blue and red bronzes by the hydrothermal treatments of H_xMoO_3, and found

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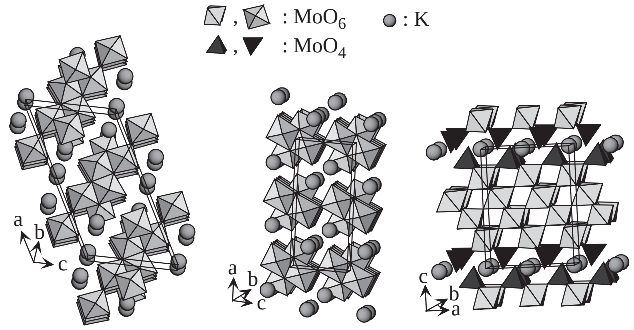

Fig. 1. Structures of alkali metal molybdenum bronzes: blue bronze (a), red bronze (b), and purple bronze (c).

that the conversion of H_xMoO_3 ($x > 0.3$) during the hydrothermal reaction was quite different from that of H_xMoO_3 ($x < 0.3$). According to our investigations of their conversion mechanisms, the difference was related to the presence of two types of conversion routes: one is a structure-inheriting solid-state route and the other is a solution dissolution/deposition one. Here we report the details of the hydrothermal syntheses and mechanisms of formation of the potassium molybdenum oxide bronzes.

2. Experimental

Materials preparation: The H_xMoO_3 ($0.25 < x < 1.34$) starting material was prepared as reported previously [19] as was the $(K\cdot nH_2O)_{0.25}[H_yMoO_3]$ (n = ca. 2) used in the present study [12,14].

Hydrothermal treatment: The starting solid suspended in 30 mL of aqueous KCl solution was placed into a 60 mL of Teflon-lined autoclave, and then heated in a forced convection oven at 431 K and autogeneous pressure. The specific solids, amounts and time are discussed in the next section. After heating, the autoclave was taken out from the oven and cooled down by an electrical fan. The resulting products were filtered, washed several times with distilled water, and dried in air.

Measurements: The powder X-ray diffraction (XRD) patterns of the samples were measured using a Mac Science MXP3VZ X-ray diffractometer with Cu$K\alpha$ radiation. Scanning electron micrograph (SEM) images of the samples were obtained in a JEOL JSM-5610LVS scanning electron microscope. The composition of the product was analyzed by a HITACHI 180-80 atomic absorption spectrometer using the 313.3 nm line for Mo, 766.5 nm line for K, and by the method of Choain and Marrion [20]. Infrared spectra were measured using a Perkin Elmer Spectrum 2000 FT-IR spectrometer.

3. Results and discussion

3.1. Products obtained by hydrothermal syntheses

Fig. 2 shows the XRD patterns of the products obtained after the hydrothermal heating of the single-phase H_xMoO_3 (1.3 g) with $x = 0.25-1.34$ (mean oxidation state of Mo (M.O.S.Mo) $= 5.75$–4.66) in 1.8 M KCl solution at 431 K for 48 h. The phases obtained are summarized in Table 1. According to the results, two kinds of potassium metal bronzes, blue and red bronzes, were formed in the present hydrothermal syntheses, but the purple bronze, containing tetrahedral MoO_4 units, was not obtained. There is seemingly a dividing line at M.O.S.Mo $= 5.70$ below which the blue bronze is formed and the red bronze is formed above it.

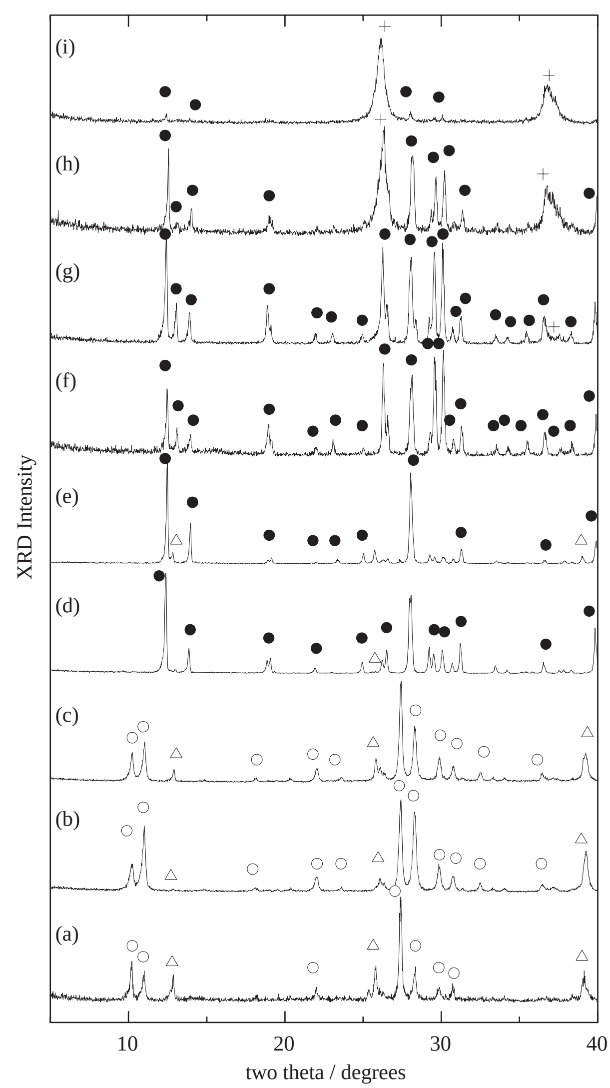

Fig. 2. XRD patterns of the products obtained by the hydrothermal treatments of H_xMoO_3 with various x values: $x = 0.25$ (a), 0.28 (b), 0.29 (c), 0.30 (d), 0.31 (e), 0.36 (f), 0.47 (g), 0.91 (h), and 1.34 (i), respectively. Symbols ○, ●, △, and + indicate blue bronze, red bronze, MoO_3 and MoO_2, respectively.