New Family Member of Hydrogen Molybdenum Bronze, H_xMoO_3

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We found out a new family member of hydrogen molybdenum bronze, H_xMoO_3. The phase exhibited the monoclinic system and appeared as a single phase in the region of 0.45>x>0.25. Its interlayer spacing varied largely depending on the hydrogen content.

Hydrogen molybdenum bronzes H_xMoO_3 are hydrogen insertion compounds of layered molybdenum trioxide. They have great technological interest due to their intense color, conductivity properties, and structural features (layer structure etc.) that make them suitable for applications such as electrochromic devices, fuel cells, functional catalysts and so on.[1,2] Recently interesting electronic and/or magnetic behaviors such as CDW[3] and spin glass[4] states etc. have been found in some of them, and they still have great scientific interest. Because of the technological and the scientific interests, we have also been studying on these compounds for long time. So far, it has been known that they exhibit four types of phases with the homogeneity of approximate limits: (**I**) blue orthorhombic, 0.23<x<0.40; (**II**) blue monoclinic, 0.85<x<1.04; (**III**) red monoclinic, 1.55<x<1.72; and (**IV**) green monoclinic, x=2.0.[5-9] However, from our experience we have been wondering if there is an additional phase in the region between phases I and II. That is, we have noticed that a phase somewhat different from phase **II**, which gives a X-ray diffraction peak in the lower angle side of the 200 peak (*d* =ca. 0.7 nm) of phase II, is formed when phase II turns to phase I by oxidation, although the phase has not been confirmed clearly, and not been prepared as a single phase. Recently, we have found a preparation route where phase III with uniformed particle size was formed from phase I by using a leaching technique.[10] Because of expectation for homogeneous reaction due to its uniformed particle size, we investigated the structural changes during the oxidation of the phase III in order to confirm the additional phase. Then, we succeeded to prepare the additional phase as a single phase. In this paper we will present the findings briefly.

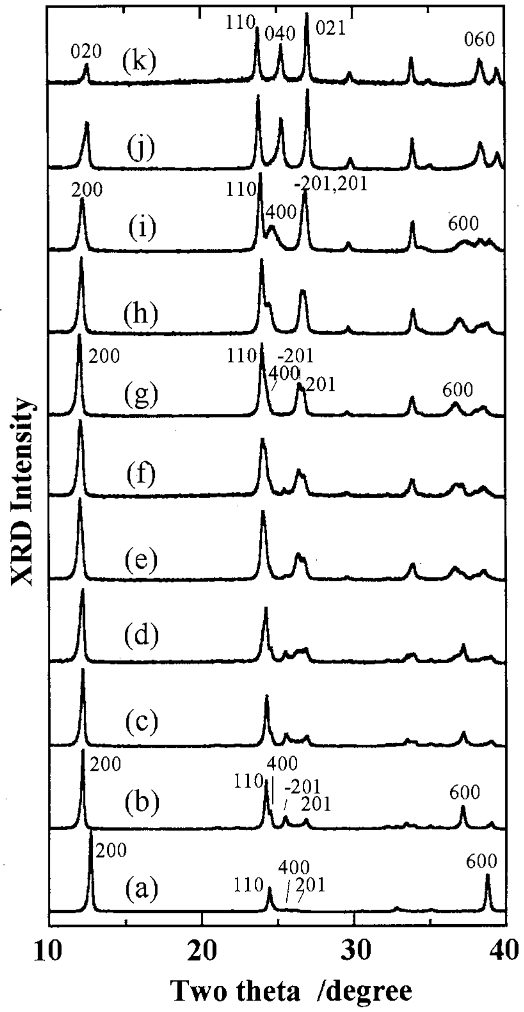

Figure 1. Changes in XRD pattern of the sample with varying hydrogen content x: (a) x=1.42, (b) x=0.79, (c) x=0.68, (d) x=0.59, (e) x=0.53, (f) x=0.45, (g) x=0.43, (h) x=0.38, (i) x=0.33, (j) x=0.26, and (k) x=0.25.

The phase **III** sample was prepared by treating phase I with Cs_2CO_3 aqueous solution at 353 K in air-free atmosphere using a hand-made apparatus composed of vacuum- and N_2-lines to prevent oxidation. According to scanning electron microscopic investigation, the sample was composed of uniformed rectangular crystallites with ca. 1 μm of side length. Oxidation of the sample was investigated in an ambient atmosphere. According to the results, the sample turned into phase I within a month. This indicates that its oxidation occurs rather faster than that for the ordinary phase III sample (usually, it takes several months), which was prepared directly from MoO_3 by chemical reduction and composed of rectangular crystallites with ca. 5 - 20 μm of side length. The rapid oxidation for the present sample may be due to its smaller particle size. Figure 1 shows the changes in XRD pattern with the hydrogen content during the oxidation of the present phase III sample. According to identification based on JCPDS database, its oxidation proceeded as Phase III (x = ca. 1.4, red)→ Phase II (x=0.8-0.6, blue) → ? (0.60>x>0.25, blue) → phase I (x=ca. 0.25, blue). And in the region of 0.60>x>0.25 unidentified XRD patterns were observed. From inspection (Figure 1), the region (0.60>x>0.25) could be divided into two sub-regions; one where only relative intensities of XRD peaks vary (0.60>x>0.45) and the other where peak positions also change (0.45>x>0.25). The peaks of phase II and those observed in the XRD pattern of the sample with x=0.43 seems to be superposed on the XRD patterns of the samples with 0.60>x>0.45, and these samples are suggested to be mixtures. On the other hand, the changes in the XRD pattern with varying x from 0.45 to 0.25 are characterized by continuous shifts to the lower angle side of the three peaks at 12.0-12.8°, 24-25.5°, and 36.0-39.0°; and by gradual removal of splitting of peaks at 26.0-27.0°. We tried to index the peaks appeared in the XRD patterns of the samples (0.45>x>0.25), and could succeed. They were all indexed with monoclinic systems. Figure 2 shows their lattice constants together with those of other phases observed as a single phase in Figure 1. The indices of main XRD peaks of the phases are shown in Figure 1. From these results, it is clear that for the above-mentioned changes in the XRD pattern of the region 0.45>x>0.25 are due to shortening of interlayer spacing (*a*/2 for the monoclinic phases and *b*/2 for the orthorhombic phase)[8] and the change in crystal system from 'monoclinic' to 'orthorhombic'. From the continuous changes in XRD pattern with varying hydrogen content, the compounds with 0.45>x>0.25 are suggested to belong to the same phase. Furthermore, the phase is concluded to be different from the phase II, because of existence of compositional gap in hydrogen content and discontinuity in interlayer spacing between phase II and it, although the two phases have the same crystal system and color. The known phases observed in the present work had somewhat lower hydrogen contents than those in literatures.[5-9] We have examined the samples' compositions many times and confirmed that the observed values were correct. We suppose that the lower values are due to the smaller particle size of the sample, and further investigation will be done in future.

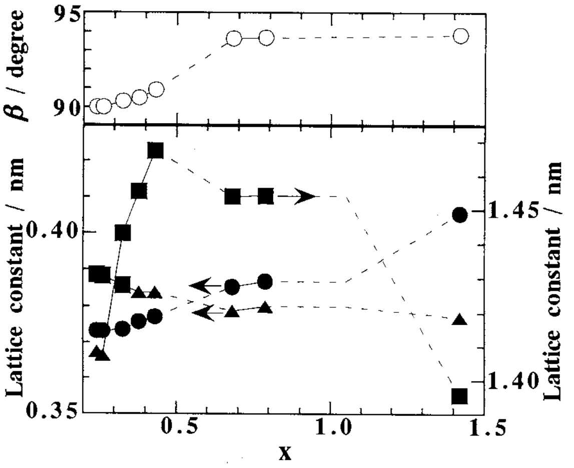

Figure 2. Changes in lattice constants with varying hydrogen content x: ■, ▲, ●, and ○ are lattice constants *a*, *b*, *c*, and *β*, respectively.

In the present work, we found out a new family member of hydrogen molybdenum bronze. The phase has large variation in its interlayer spacing and can take the same hydrogen content as the phase with a CDW[3] or a spin glass[4] state, exhibiting the different structure. These findings will provide interesting subjects of material science.

References and Notes

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