HRTEM STUDIES OF TWO NEW (Nd, Ca)_xWO_3 BRONZES SYNTHESIZED UNDER HIGH PRESSURE CONDITIONS

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(Received November 13, 1995; Communicated by A. Magneli)

ABSTRACT

Two new (Nd, Ca)_xWO_3 bronzes have been prepared by solid state reaction at \( P = 50 \) kbar and \( T = 1520 \) K. The compounds were studied by X-ray powder diffraction and high resolution transmission electron microscopy. One phase was identified to be of hexagonal tungsten bronze type, while the other one was found to have the intergrowth tungsten bronze structure (2)-ITB. Disorder in terms of varying widths of the HTB and WO_3 slabs was sometimes observed. HTB tunnel rows terminating in the (2)-ITB structure were also seen. The neodymium and calcium contents in the two phases were confirmed by EDS analysis.

KEYWORDS: A. oxides, C. electron microscopy, C. high pressure, D. crystal structure, D. defects.

INTRODUCTION

By experiments at high pressures \((P = 50-80 \text{ kbar})\) and temperatures \((T = 1120-1770 \text{ K})\), it has been possible to prepare several new reduced tungsten oxide phases. Four of these have been studied by X-ray and electron crystallographic techniques. The new phases include WO_{2.625}...
(W₈O₂₁) (1), two modifications of W₃O₈ (I and II) (2,3) and a hp-WO₂ modification (4). These studies show that the phase conditions of the tungsten-oxygen system at high pressure deviate considerably from those at ambient pressure. It was therefore considered to be of interest to perform high-pressure experiments on some ternary metal-tungsten-oxygen systems. This paper describes some results of investigations of the neodymium-tungsten-bronze system.

There is not much data in the literature concerning tungsten bronzes of rare earth elements. Some perovskite-type phases RE₂WO₅ have been reported to form by solid-state reaction at high temperature (T = 1300 K) and ambient pressure (5-7).

EXPERIMENTAL

The synthesis was performed using a high-pressure equipment developed at the Institute for High Pressure Physics at Troitsk. A detailed description of the experimental set-up is given under preparation and will be presented elsewhere.

The sample was prepared from a weighed-in mixture of 10 wt% Nd₂O₃ and 90 wt% WO₃, which was thoroughly ground in an agate mortar and pelletized. The pellet was heated in a graphite container in the high-pressure toroid-type limestone chamber at P = 50 kbar and T = 1520 K for 3 minutes. The temperature difference between the central and edge parts of the sample was less than 50°C. The calcium content of the samples discussed below is obviously due to contact with the chamber wall.

The X-ray powder diffraction pattern was taken with a Guinier-Hägg camera using CuKα₁ radiation and silicon as an internal standard.

The electron microscopy specimens were prepared by crushing a small amount of the sample in an agate mortar, dispersing the resulting fine powder in acetone, and putting a few drops of the suspension onto a holey carbon film supported on a copper grid. The JEOL ARM microscope operated at 800 kV (NCEM Berkeley) was used. High resolution transmission electron microscopy (HRTEM) images were taken from thin crystal fragments aligned so that the crystal c-axis was parallel to the electron beam. The radius of the objective aperture used was 0.72 Å⁻¹. An Akashi 002B transmission electron microscope equipped with a LINK EDS-system was used for qualitative analysis.

RESULTS AND DISCUSSION

The electron microscopy investigation showed a multi-phase sample, with two predominant phases of bronze-type structures. Both could be seen in the X-ray powder pattern.

Hexagonal tungsten bronze (HTB). One of the phases was identified from the electron diffraction pattern and the HRTEM image to be of hexagonal tungsten bronze (HTB) type. The unit cell dimensions calculated from the X-ray powder data are a = 7.395 Å and c = 7.585 Å. These values are in reasonable agreement with those reported for the alkali tungsten bronzes A₂WO₅ with A = Rb and Cs (8,9). In the HTB structure, the A atoms occupy sites in the six-sided tunnels. The theoretical upper limit of x is 0.33, which corresponds to full occupancy of all sites
in these tunnels. From the low magnification image in Figure 1, one can easily notice obvious differences in contrast among the hexagonal tunnels, which indicate considerable variation of their contents of metal atoms. In the EDS spectra taken from such crystals, small peaks from Nd and Ca were observed. No sign of superstructure reflections, which could indicate an ordering of the tunnel ions and vacancies, was found in the electron diffraction patterns. This means that the metal atoms in the tunnels are probably randomly distributed. However, superstructures in HTB have previously been reported for tungsten bronzes with alkali \((10,11)\) and indium \((12)\) and also for the bronzoid with cesium, \(\text{Cs}_2(\text{W,Nb})\text{O}_3\) \((13)\). The latter is a fully oxidized analogue of hexagonal tungsten bronze, with niobium substituting for the proper amount of tungsten \((13)\).

![Low magnification micrograph of a thin crystal fragment in [001] projection, showing variation of filling of the tunnels in the HTB structure.](image)

A few defects have been observed in the HTB structure. One example is illustrated in Figure 2. The low-magnification micrograph (Fig. 2a) is taken of a rather thick, not perfectly aligned HTB crystal. Here, thin slabs of \(\text{WO}_3\)-type structure, two and three octahedra wide, are intergrown with the HTB structure. Figure 2b shows the corresponding structure model.

**Intergrowth tungsten bronze (ITB).** The HRTEM image shown in Figure 3a is taken from a thin crystal of the second phase. The unit cell dimensions calculated from the X-ray powder data are \(a = 10.138\ \text{Å},\ b = 7.423\ \text{Å},\ \text{and}\ c = 3.792\ \text{Å}.\) The black contrast features in the image correspond to the model in Figure 3b, i.e., an intergrowth tungsten bronze (ITB) type structure. According to the nomenclature of the ITB families of related phases introduced by Hussain and Kihlborg \((14)\), the structure shown in Figure 3b is denoted \((2)\)-ITB and belongs to the \((n)\)-ITB family of related phases. The number \(n\) corresponds to the number of \(\text{WO}_6\)-octahedra across the \(\text{WO}_3\)-type slabs in the structure. The theoretical upper limit of \(x\) for the \((2)\)-ITB phase is 0.20. The \((2)\)-ITB structure can be considered to consist of HTB slabs, one single hexagonal tunnel row wide, which are mutually linked by corner-sharing. The \((2)\)-ITB phase has been observed in the \(\text{Sb}_x\text{WO}_3\) system \((15)\). EDS analysis showed the presence of both Nd and Ca in most of the examined crystal fragments. The HRTEM image suggests different degree of filling of the six-sided tunnels. Some tunnels look almost empty (bright) while others seem to be fully occupied (black spots). No superstructure reflections were found in the electron diffraction patterns. This indicates random occupancy of the metal atom sites in the hexagonal tunnels.
FIG. 2
(a) Low magnification image ([001] zone) showing isolated faults of WO₃-type structure in an HTB crystal. (b) Idealized structure model of the defect region to the left in (a). The figures refer to the number of octahedra (width) in the WO₃ slabs.

FIG. 3
(a) HRTEM image of a thin crystal of (2)-ITB phase projected along the $c$-axis. (b) Corresponding structure model, (2)-ITB. The sites in the six-sided tunnels are indicated by filled circles.
Various kinds of disorder and intergrowth structures were observed in the examined crystals. One example is shown in Figure 4. Here, slabs consisting of two or even three hexagonal tunnel rows are seen as defects in a crystal, which is essentially (2)-ITB. Another type of defect is marked by an arrow. Here, an extra layer of corner-sharing \( \text{WO}_6 \)-octahedra is incorporated into the host structure, thus forming a three-octahedra-wide \( \text{WO}_3 \)-type slab. An idealized structure model of the region, marked in Figure 4a, is shown in Figure 4b. The model illustrates a narrow region of (1,2)-ITB phase intergrown with the (2)-ITB structure. The (1,2)-ITB structure is characterized by HTB elements, two hexagonal tunnel rows wide, and \( \text{WO}_3 \)-type slabs, two octahedra wide. The (1,2)-ITB structure has previously been observed in the \( \text{Sn}_x \text{WO}_3 \) bronze system (16,17). The general formula for this family of related structures is (1,\( n \))-ITB (14) and is the most common one in the alkali system.

The HRTEM study of the (2)-ITB bronze phase also showed isolated defects consisting of HTB-type slabs of different width incorporated into the ordered (2)-ITB structure. The widest slab observed is 45 Å thick, corresponding to seven rows of hexagonal tunnels (Fig. 5). The HTB structure is not strictly hexagonal inside this slab but is slightly distorted probably due to elastic stress; the distance between the hexagonal tunnels along the slab is about 3% larger than that measured at the 60° angle to the slab axis. As a result, the angle between rows of tunnels in the slab is 121.8°.
Another type of defect is illustrated in Figure 6. Here a slab, three hexagonal tunnel rows wide, terminates in the (2)-ITB structure (Fig. 6a). An idealized structure model of the fault region is illustrated in Figure 6b. The image and the model show that the HTB tunnel row in the middle terminates is a five-sided tunnel (see arrows). Such termination of HTB tunnel rows in a WO$_3$ matrix has been previously suggested for ITB bronzoids (13).

In the present investigation, no ordered member of the (n)-ITB family of width $n>2$ has been observed so far. Such phases have been reported for the tungsten bronzes of barium, tin and lead (17) and are also found in alkali tungsten bronze samples with low alkali content (18). Neither has any ordered member of the (1,n)-ITB family, with double tunnel rows, been observed in the investigated samples. Such structures have only been observed to exist as defects in (2)-ITB.

The content $x$ in the bronze phases, (Nd,Ca)$_x$WO$_3$, is associated both with the number of hexagonal tunnels in relation to the number of tungsten atoms in the structure and with the
occupancy of the tunnel sites. The HRTEM study presented above indicates that it might be
difficult to determine the composition regions for the ITB and HTB phases, because defects,
disorder and variable tunnel occupancies were frequently observed in the examined crystals.
However, EDS analysis in combination with electron diffraction and, if possible, HRTEM
images taken of the same fragment might give valuable information in this field.

The first quantitative results obtained from an EDS study of a few crystals indicated an Nd
and Ca content, both less than 0.1, for both the ITB and HTB phases. A more extensive study of
several samples of different bulk compositions, prepared under slightly different experimental
conditions, is under way. Such a study might also give valuable information about the formation
mechanism of the tungsten bronzes under high pressure conditions.

ACKNOWLEDGMENTS

We wish to thank Professor A. Magnéli for stimulating discussions and valuable comments
on the manuscript. The use of the facility at the National Center for Electron Microscopy at the
Lawrence Berkeley Laboratory is greatly appreciated. This study has partly been performed
within a program for Swedish-Russian joint research projects. Financial support from the Royal
Swedish Academy of Sciences and from the Swedish Natural Science Research Council is
gratefully acknowledged. The research described in this publication was made possible in part by
Grant No NFP000 from the International Science Foundation.

REFERENCES

2. M. Sundberg, N.D. Zakharov, I.P. Zibrov, Yu.A. Barabanenkov, V.P. Filonenko and
    (1979).