The structure of a new calcium intergrowth tungsten bronze, Ca$_x$WO$_3$, prepared at $P = 80$ kbar and $T = 1670$ K, has been studied by high-resolution transmission electron microscopy and supplementary techniques. The unit-cell dimensions, determined from X-ray powder data, are: $a = 10.1500(9)$, $b = 7.4232(7)$ and $c = 3.7915(4)$ Å. The crystal structure is of ($n$)-ITB type with $n = 2$. It is isotypic with those recently reported for the RE$_x$WO$_3$ bronzes ($RE =$ Pr and Nd) prepared at $P = 50$ kbar. Combined electron diffraction and energy-dispersive X-ray spectroscopy (EDX) studies of thin crystallites showed that the hexagonal tunnels were less than half-filled with Ca atoms ($x \approx 0.07 \pm 0.01$). Electron diffraction patterns revealed ordered superstructures of (2)-ITB as well as an order–disorder transformation under the intense electron beam. A calcium bronze ($Ca \approx 0.12 WO_3$) with an hexagonal tungsten bronze structure (HTB) was also observed in the sample.

Keywords: calcium tungsten bronze, high-resolution transmission electron microscopy, high-pressure synthesis, microanalysis, crystal structure, order-disorder

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1. Introduction

The crystal structures of transition metal oxides containing niobium and tungsten have turned out to be very sensitive to the application of high pressure during synthesis. Several new binary oxides have been prepared at high pressures, $P=50–80$ kbar, and temperatures of $T>1500$ K [BARABANENKOV et al., SUNDBERG et al., ZIBROV et al.].

Similar high-pressure experiments in the systems Nd$_2$O$_3$–WO$_3$–W and Pr$_2$O$_3$–WO$_3$–W have shown that both hexagonal tungsten bronze (HTB) and intergrowth tungsten bronze (ITB) structures are formed in the samples prepared at $P = 50$ kbar [ZAKHAROV et al. 1996, ZAKHAROV et al. 1999]. In the latter system ordered Pr$_x$WO$_3$ bronzes of ($n$)-ITB structure type with $n = 2$, 3 and 4 have been identified from high-resolution transmission electron microscopy (HRTEM) images. According to the microanalysis results, the hexagonal tunnel sites were less than half-filled with praseodymium ions. Tungsten bronzes from the neodymium-containing sample have been denoted (Nd,Ca)$_x$WO$_3$, because the energy-dispersive X-ray spectroscopy (EDX-results) showed most of the examined fragments to contain some amount of calcium due to reaction with the high-pressure cell material. HRTEM studies of such crystals have revealed ordered and disordered structures of HTB and (2)-ITB types. Furthermore, Ca$_x$WO$_3$ bronzes of HTB type have been prepared hydrothermally and under high-pressure conditions (60–65 kbar) [BIERSTEDT et al., BITHER et al.].

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Structural Studies of Calcium Tungsten Bronzes, Ca$_x$WO$_3$, Formed at High Pressure

Dedicated to Prof. Dr. J. Heydenreich on the occasion of his 70th birthday
In view of the results obtained on the (Nd,Ca)\(_x\)WO\(_3\) bronzes, we have synthesised a few Ca\(_x\)WO\(_3\) samples at elevated pressures. The present study deals with HRTEM and EDX investigations of one of these samples. The ordered and defect structures of a new calcium intergrowth tungsten bronze will be presented and discussed.

2. Experimental

A sample of composition Ca\(_{0.1}\)WO\(_3\) was prepared from appropriate amounts of dried CaO, WO\(_3\) and W metal powder by grinding the starting materials thoroughly in an agate mortar, both as dry powders and under acetone. The resulting product was pressed into a pellet, which was wrapped up in a tungsten foil. The pellet was then heated for 5 minutes in a graphite container in a high-pressure cell at \(P = 80\) kbar and \(T \approx 1670\) K. The high-pressure equipment and the experimental procedure have been described previously [ZIBROV et al.].

An X-ray powder diffraction pattern was taken in a Guinier–Hägg camera, using monochromatized CuK\(_\alpha\) radiation and Si as internal standard. The electron microscopy specimens were prepared by crushing a small amount of the sample in an agate mortar, dispersing the fine powder in acetone and putting a drop on a perforated carbon film supported on a Cu grid. The phase composition and the structure type of the thin crystallites were investigated by combining selected-area electron diffraction and energy-dispersive X-ray spectroscopy (EDX). The ordered and defect structures were explored by high-resolution transmission electron microscopy (HRTEM). The electron microscopes used were a Philips CM20T equipped with EDX (Voyager I, Ge detector) and a JEOL JEM-4000EX. The DigitalMicrograph 2.0 software was used for image filtration and processing. Theoretical images of the crystal structure were simulated with the MacTempas program [KILAAS].

3. Results

The X-ray powder pattern showed a multiphasic sample. Lines characteristic of the tungsten bronzes (2)-ITB and HTB could be identified in the X-ray pattern, and the unit-cell parameters of the two compounds were refined from the X-ray data. The following unit-cell dimensions were obtained: (2)-ITB) \(a = 10.1500(9)\), \(b = 7.4232(7)\) and \(c = 3.7915(4)\) Å and (HTB) \(a = 7.4077(5)\) and \(c = 7.5787(6)\) Å. These values are very close to those previously reported for the (Nd,Ca)\(_x\)WO\(_3\) bronzes of (2)-ITB and HTB structure types [ZAKHAROV et al., 1996].

3.1. Hexagonal tungsten bronze (HTB)

Electron diffraction patterns have been recorded from over fifty crystallites. Only one of these (Fig.1a) was of HTB structure type. The crystal structure of the hexagonal tungsten bronze, \(A\)WO\(_3\), is shown in Fig.1b. When all hexagonal tunnel sites are completely filled by \(A\) atoms the value of \(x\) is equal to 0.33. According to the EDX results the composition of the crystallite was close to Ca\(_{0.12}\)WO\(_3\), which means that approximately 1/3 of the hexagonal tunnels sites were occupied by Ca atoms (ions). The weak streaks running in the \(<100>\) directions in the ED pattern (Fig.1a) illustrate disorder in the structure, which is most likely due to intergrowth of HTB regions with thin slabs of the (2)-ITB phase. The latter intergrowth has been seen in HRTEM images taken of HTB crystals of (Nd,Ca)\(_x\)WO\(_3\) [ZAKHAROV et al.,1996].

3.2. Intergrowth tungsten bronze, (2)-ITB

ED patterns characteristic of (2)-ITB crystals dominated in the recorded patterns. A typical HRTEM image of a thin (2)-ITB crystallite with the corresponding ED pattern inserted is
illustrated in Fig. 2. The image was taken close to Scherzer resolution, which means that the dark spots correspond to projected cation positions. There is a good agreement between the arrangement of dark spots in the HRTEM image and the tungsten atom arrangement in the structure model of (2)-ITB in Fig. 3a. The ReO\textsubscript{3} slabs, two octahedra wide, correspond to the thin lamellas consisting of two rows of black spots in the image. The HTB slabs, one hexagonal tunnel row wide, are clearly seen in the thin part at the crystal edge in Fig. 2. A defect consisting of three adjacent HTB tunnel rows is marked. The micrograph also illustrates that there is a variation in the filling of the hexagonal tunnel sites with calcium. Some tunnels seem to be empty (white spots) while others are more filled (darker contrast). In the thinner region these variations of tunnel intensity is much less pronounced, due to the low atomic scattering amplitude of Ca. In the Fourier-filtered image of a small region at the crystal edge (Fig. 3b), the hexagonal tunnels look like bright six-fold stars with symmetric dark contrast. The tungsten atom positions, deduced from the processed image, are almost identical to those recently given for Pr\textsubscript{x}WO\textsubscript{3} of (2)-ITB structure type [ZAKHAROV, et al., 1999].

Fig. 1: a) ED-pattern from an HTB crystal, Ca\textsubscript{3}WO\textsubscript{3}, in [001] projection. Streaking in the <100> directions indicates the presence of some disorder.

b) Crystal structure of hexagonal tungsten bronze, A\textsubscript{2}WO\textsubscript{3}, [MAGNÉLI]. The A atom positions in the six-sided tunnels are marked by weak spots.

Fig. 4 illustrates two types of ED pattern taken from thin crystal fragments in [010] projection. They show both the same basic cell with \(a \approx 10.1\) Å and \(c \approx 3.8\) Å. In Fig. 4a, only the reflections characteristic of basic cell are seen, whereas weak superstructure reflections are revealed in the ED pattern in Fig. 4b. These reflections indicate doubling of the \(a\) and \(c\) axes, and thus unit cell parameters of \(a = 2 \times 10.1 = 20.2\) Å and \(c = 2 \times 3.8 = 7.6\) Å. The ordered superstructure of (2)-ITB may be caused by some features in the oxygen arrangement or to an ordered arrangement of calcium atoms and vacancies in the six-sided tunnels. Similar types of superstructure reflections have been observed in electron diffraction patterns taken from the alkali intergrowth tungsten bronzes [KIHLBORG].

Superstructure reflections were also often observed in ED patterns taken along [001]. In the two examples in Fig. 5, the same basic cell with the parameters \(a \approx 10.1\) Å and \(b \approx 7.4\) Å can be seen. In both patterns the weak superstructure reflections indicate a doubling of the parameters, and thus the lattice dimensions are \(a \approx 2 \times 10.1 = 20.2\) Å and \(b \approx 2 \times 7.4 = 14.8\) Å. The superstructure reflections are sharp in Fig. 5a, indicating an ordered superstructure of (2)-ITB-type. Streaking of the reflections \(h+k = \text{odd}\) along [010] in Fig. 5b suggests a disordered arrangement of calcium atoms and vacancies along the \(b\) axis.

Similar type of ED pattern as the one in Fig. 5a has been taken from Pr\textsubscript{x}WO\textsubscript{3} crystals of (2)-ITB structure type [ZAKHAROV, WERNER et al.]. It has not been possible, however, to record the corresponding HRTEM images, because the crystals were not stable under the high intensity of the electron beam used to get the image. In the present study we were able
to take the set of ED patterns in Fig. 6, showing the order–disorder transition. Fig. 6a is taken from a thin crystal fragment before the crystal was irradiated with an intense electron beam. It shows superstructure reflections of the same type as in Fig. 5a. The ED pattern in Fig. 6b shows that the superstructure reflections have disappeared due to the irradiation of the crystal with an intense beam for a very short time. The ED pattern in Fig. 6c is taken from the same region of the crystal about half a minute after the beam intensity was decreased. The weak superstructure reflections reappear in the pattern, indicating an ordered superstructure of (2)-ITB.

Fig. 2: HRTEM image of a thin (2)-ITB crystal aligned along the 3.8 Å axis, with the corresponding ED pattern inserted. The dark spots correspond to cation positions. A defect of HTB type is marked by an arrow. Abnormally bright hexagonal tunnels, presumably empty, are marked by E.

Fig. 3: a) The crystal structure of (2)-ITB in [001] projection. The Ca atoms (dark spots) are located in the six-sided tunnels in the HTB-type slabs. b) Fourier-filtered image of a small region close to the crystal edge in Fig. 2.
Fig. 4: ED patterns of (2)-ITB projected along the $b$ axis showing: a) the basic cell b) the basic cell with weak superstructure reflections.

Fig. 5: ED patterns of (2)-ITB in [001] projection showing: a) the basic cell with weak superstructure reflections b) the basic cell with weak superstructure reflections and streaking of the reflections along [010].

Fig. 6: A set of ED patterns taken from a (2)-ITB crystal aligned along [001] illustrates an order–disorder phase transition. The displayed ED patterns are taken a) before b) just after and c) about half a minute after irradiation of the fragment by a 200 kV intensive electron beam. The weak superstructure reflections seen in the ED pattern in a) have disappeared in the ED pattern in b) and re-appear in the ED-pattern in c).

The stoichiometric composition of the (2)-ITB structure in Fig. 3a is $\text{CaW}_5\text{O}_{15}$ when all hexagonal tunnel sites are occupied with calcium. This means that the $x$ value in the formula $\text{Ca}_x\text{WO}_3$ cannot exceed 0.2. Twenty-three crystal fragments of the (2)-ITB type structure were analysed by combination of electron diffraction and EDX studies. Thirteen ED patterns showed the basic unit cell without superstructure reflections. The Ca content in these crystals varied in the range $0.04 \leq x \leq 0.086$ with an average content of $x \approx 0.068 \pm 0.011$. The results show that between 20% and 45% of the hexagonal tunnel sites are filled by calcium atoms. One crystal fragment exhibited a very high Ca content, $x = 0.15$, corresponding to 75% occupancy of the six-sided tunnel sites. The ED-patterns from the remaining ten crystallites exhibited weak superstructure reflections like the ones shown in Fig.5a. The Ca content of
these crystals was very much the same: in the range $0.05 \leq x \leq 0.10$ with an average content of $x = 0.075 \pm 0.011$. However, the weak superstructure reflections might indicate a displacement of the Ca atoms from the tunnel axis or an ordered arrangement of Ca atoms and vacancies in the hexagonal tunnels.

The HRTEM image in Fig.7 illustrates some typical defects in the (2)-ITB structure of CaWO$_4$. An ReO$_3$-type slab, three octahedra wide, can be seen to the left, and HTB-type slabs two and three hexagonal tunnel rows wide are marked in the image. According to the nomenclature given by HUSSAIN et al., single hexagonal tunnel row structures are denoted $(n)$-ITB, whereas double and triple hexagonal tunnel row structures are indicated by $(1,n)$-ITB and $(1,1,n)$-ITB, respectively. The width of the ReO$_3$-type slab separating the hexagonal tunnel rows is given by $n$. Most of the defects in Fig.7 can be considered as intergrowths of thin slabs of the $(1,1,2)$-ITB and the $(1,2)$-ITB structures with the (2)-ITB phase. The Ca content in these defect regions is probably somewhat higher than that in an ordered (2)-ITB crystal, as the number of available hexagonal tunnels where the Ca atoms can enter has increased.

4. Discussion

The results presented above clearly show that calcium bronzes of $(n)$-ITB and HTB structure types are formed at the synthesis pressure of 80 kbar. Ordered and disordered crystals of (2)-ITB were observed, usually with less than 50% of the hexagonal tunnel sites occupied by calcium ions. There is no indication of perovskite tungsten bronze (PTB) or tetragonal tungsten bronze (TTB) type structures in the examined sample. Calcium bronzes of HTB type have previously been prepared at $P = 60–65$ kbar [BITHER et al.], whereas PTB and TTB type structures of CaWO$_4$ have been synthesised under ambient pressure conditions [VANDEVEN et al., WACHSMANN et al.]. It is well known that the size of the tunnel ion has a great influence on the formation of the structure type. The ionic radius of Ca$^{2+}$ ($r = 1.34$ Å) is much less than that of Ba$^{2+}$ ($r = 1.61$ Å) [SHANNON]. The latter element forms barium intergrowth tungsten bronzes of approximate composition Ba$_{0.04}$WO$_3$ with $(n)$-ITB structures under ambient pressure conditions [EKSTRÖM et al.]. The WO$_3$-slabs are $n = 8$–13 octahedra wide, and more than 70% of the hexagonal tunnel sites are filled with barium ions. The WO$_3$ slabs are thus wider and the degree of filling of the hexagonal tunnel higher than in the analogous calcium bronzes. By applying pressure during the synthesis of the CaWO$_3$ bronzes, the hexagonal tunnels will be slightly compressed and thus more favourable for the calcium atoms. However, the minimum pressure and temperature needed to form calcium bronzes of ITB- and HTB-type structures are still unknown.

The results obtained on the CaWO$_3$ bronzes above are similar to those previously observed for the (Nd,Ca)$_x$WO$_3$ bronzes [ZAKHAROV et al., 1996] although the preparation conditions differ. The Ca content in the latter bronzes was due to contamination from the high-pressure cell material. Both Ca$_x$WO$_3$ ($P = 80$ kbar) and (Nd,Ca)$_x$WO$_3$ ($P = 50$ kbar) form ordered and disordered bronzes of (2)-ITB type, and the hexagonal tunnel sites are less than half-filled with Ca and Nd/Ca respectively. The ionic radius of Nd$^{3+}$ ($r = 1.27$ Å) is only slightly less than that of Ca$^{2+}$ ($r = 1.34$ Å), and it is obvious that the two ions can replace each other in the hexagonal tunnels.

There are some indications in the HRTEM image that the Ca atoms might be displaced from the hexagonal tunnel axis. Previous X-ray diffraction studies of K$_2$WO$_3$ have shown that off-centre displacements of the potassium atoms occur in the HTB-type structure [KIHLBORG et al.]. A shift of In$^{1+}$ from the hexagonal tunnel axis in the HTB structure of In$_x$WO$_3$ has also been reported by LABBÉ et al. They found that the indium cations could occupy one of six off-centre positions in the tunnels. However, this was considered related to the presence of
the lone-pair electrons on In$^{1+}$. We have recently reported that the hexagonal tunnels in the praseodymium ($n$)-ITB bronzes are elongated along the 7.4 Å axis [ZAKHAROV et al., 1999]. The elongation gives rise to two off-axis positions where the praseodymium atoms seem to enter. A similar displacement has not been seen in the present study.

According to the microanalysis results above, the observed superstructure of (2)-ITB does not seem to be related to the Ca content of the crystals, but is probably due some feature in the oxygen arrangement and to the location of the calcium atoms in the hexagonal tunnels. Superstructure reflections in the ED patterns may show an ordered arrangement of Ca atoms and vacancies in the hexagonal tunnels, whereas the absence of superstructure reflections indicates randomly distributed calcium atoms in the tunnels. Alternatively, it might be due to a displacement of the Ca atoms from the tunnel axis and an accompanying distortion of the WO$_6$ network. This explanation is supported by the fact that the doubled $c$ axis in the HTB structure of the alkali bronzes is caused by a displacement of the tungsten atoms from the centre of the octahedra. This off-centre displacement is analogous to the puckering of tungsten atoms that has been seen in several tungsten oxides. The order–disorder transition observed by electron diffraction is reversible and very fast. It seems most likely that the transition is due to small displacements of calcium atoms in the hexagonal tunnels due to heat from the electron beam. However, additional X-ray information is needed to establish the reason for the observed superstructure reflections in the electron diffraction patterns.
The results obtained in the present study suggest that it would be of interest to prepare some additional Ca$_x$WO$_3$ samples under different pressure and temperature conditions in order to establish the formation conditions and stability of the Ca$_x$WO$_3$ bronzes of ITB and HTB structure types. Such experiments are now under way and will be reported later.

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