

Phase Analyses of Potassium, Rubidium and Cesium Tungsten Bronzes

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The formation of the various phases of alkali tungsten bronzes, $M_x\text{WO}_3$, where $M = \text{K, Rb and Cs}$, has been investigated mainly within the temperature range 700–950 °C. Intergrowth tungsten bronzes, ITB, and hexagonal tungsten bronzes, HTB, form with all these metals: ITB for $0.06 \leq x \leq 0.10$ and HTB for $0.19 \leq x \leq 0.33$. Potassium also forms a tetragonal tungsten bronze phase, TTB, within the range $0.42 \leq x \leq 0.57$; for $x > 0.48$ it could not be prepared in the normal way from K_2WO_4 , WO_3 , and WO_2 , however, but only by hydrogen reduction of a potassium tungstate mixture. HTB forms at all temperatures investigated, ITB only above 800 °C, while the TTB phase is stable up to 900 °C and decomposes above this temperature. The relationships between composition and unit cell parameters have also been studied for the TTB and HTB phases.

The alkali metal tungsten bronzes are the best studied and longest known compounds among the oxide bronzes. They are non-stoichiometric compounds of the general formula, $M_x\text{WO}_3$, where M represents an alkali metal. As early as 1823, Wöhler¹ prepared sodium tungsten bronzes and somewhat later Laurent,² von Knorre³ and Schäfer⁴ reported the same type of compounds with potassium, lithium and rubidium, respectively. These compounds were believed to be stoichiometric until 1935 when Hägg⁵ in a systematic study using X-ray diffraction techniques found that all sodium tungsten bronzes of cubic symmetry belong to a continuous series of solid solutions. Later Magnéli and Blomberg⁶ prepared the corresponding cesium compound in a study of the alkali metal tungsten bronzes.

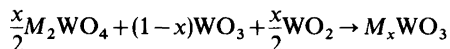
Alkali metal tungsten bronzes adopt four different types of structures. These are (i) perovskite tungsten bronzes, PTB, formed by Li and Na,^{5,6} (ii) tetragonal tungsten bronzes, TTB, with Na and K,^{5,7} (iii) hexagonal tungsten bronzes, HTB⁸ and (iv) intergrowth tungsten bronzes, ITB,⁹ the latter bronze types with K, Rb and Cs. The Li and Na atoms in PTB partially fill the A positions of the perovskite structure, ABO_3 . The symmetry is lower than cubic for low x -values. The structures of TTB and HTB are built up by corner sharing of WO_6 octahedra, which give rise to tri-, tetra-, penta- and hexagonal tunnels formed by linkage of 3, 4, 5 and 6 octahedra, respectively. The trigonal tunnels are too small to accommodate alkali atoms with the possible exception of lithium.¹⁰ The alkali atoms in TTB are located in tetra- and pentagonal tunnels^{7,11,12} and in HTB in the hexagonal tunnels.⁸ The structure of ITB can be considered as an intergrowth of WO_3 and HTB elements, which gives rise to a family of closely related phases.⁹ Each member in this family is characterized by specific thickness of slabs of the two structure elements. The alkali content is determined by two factors: the relative proportion of the HTB-type elements in the structure and the occupancy of the alkali sites in the HTB tunnels.

The perovskite type bronzes have been studied rather extensively whereas there has been no systematic study of the TTB, HTB and ITB phases formed in the K, Rb and Cs systems. This led us to undertake a thorough investigation of the phase relationship of these systems. The results are reported here.

EXPERIMENTAL

Preparation and materials. The bronzes were synthesized by the following methods:

(a) Samples of various compositions with $0.01 \leq x \leq 0.80$ were prepared from the appropriate amounts of M_2WO_4 , WO_3 and WO_2 according to the following formula:



The finely ground, intimate mixtures were introduced into silica tubes which were evacuated and sealed. The sealed tubes were heated in a furnace at various temperatures between 700 and 950 °C for periods of time ranging from 15 h to several weeks. In some cases, the samples were packed tightly in a small gold or platinum tube sealed at one end and pressed tightly or sealed at the other end. This metal tube was then placed in a silica tube, thoroughly evacuated, and sealed.

(b) Tetragonal tungsten bronzes were also prepared by reduction of polytungstate mixtures with the gross composition $K_2O \cdot nWO_3$, where $n > 1$, in a slow stream of hydrogen at 600 °C for about 40 min.⁷ The potassium polytungstate mixtures used were prepared by heating appropriate amounts of potassium tungstate and tungsten trioxide at 800 °C for one week. This method was employed to prepare tetragonal bronzes with higher alkali metal content. TTB obtained in this way was also reheated at 800, 850 and 950 °C in evacuated sealed silica tubes for a few days to a week.

K_2WO_4 was commercially available (BDH, reagent grade) whereas Rb_2WO_4 and Cs_2WO_4 were prepared from corresponding carbonate (BDH, reagent grade) and WO_3 (Koch-Light Laboratories Ltd., 99.9%, or obtained by dehydrating tungstic acids, Merck, puriss). Tungsten dioxide was prepared from WO_3 by reduction with an H_2/H_2O mixture.

Identification of the various phases. The characteristic colours of the various phases (ITB black, HTB dark blue and TTB red violet) facilitated their preliminary identification under a microscope. Definitive evidence was obtained from their X-ray powder patterns. These were recorded both before and after purification of the products with a Guinier-Hägg focusing camera using monochromatic $CuK\alpha_1$ radiation ($\lambda = 1.54051 \text{ \AA}$). KCl ($a = 6.2919 \text{ \AA}$) was used as an internal standard whenever unit cell parameters were to be calculated.

Purification. The bronzes could be purified from the unreacted material and other non-bronze phases (including possible contamination from the reaction tubes at higher temperatures). Use was made of the unusual chemical inertness of tungsten bronzes

and the purification consisted of successive treatment with boiling aqueous solution of HF (40%), conc. HCl and 10% NaOH with thorough washing with water after each step.⁶ In some cases a final treatment with *aqua regia* was employed. The remaining bronze was finally washed with alcohol and then dried at 60 °C.

Chemical analysis. The method for the analysis of the alkali metal content in tungsten bronzes has recently been reported elsewhere.¹³ Bronzes were oxidized in air at 550–600 °C and then dissolved in 1 M sodium hydroxide solution. The alkali metal content of the solution was then determined by atomic absorption spectrometry. The compositions given in this article were obtained in this way.

Since most of the syntheses were made in silica tubes under reducing conditions there is a risk of contamination by silicon. To check this two K-HTB samples prepared at 900 and 950 °C with relatively high alkali content (where the risk for contamination should be greatest) were analysed by plasma emission spectroscopy after oxidation and dissolution as above. A blank containing the same starting materials, not heat treated, was also run. All three samples gave a Si content of approximately 25 ppm. There was no significant difference between the blank and the heat treated samples in this respect, indicating that no silicon had been introduced during the annealing.

RESULTS AND DISCUSSIONS

The results of the present phase analysis are summarized in Fig. 1. The formation regions are almost the same for all the three systems (K, Rb

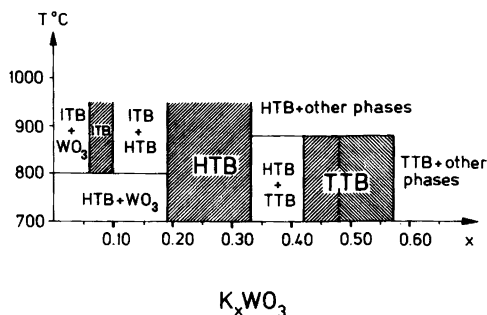


Fig. 1. Formation temperature versus potassium content for potassium tungsten bronzes (ITB: intergrowth, HTB: hexagonal and TTB: tetragonal tungsten bronzes). Rubidium and cesium have practically the same formation diagram except that they do not form a TTB phase. TTB with $x > 0.48$ (to the right of the dotted line) could be prepared only by hydrogen reduction of polytungstate mixtures.

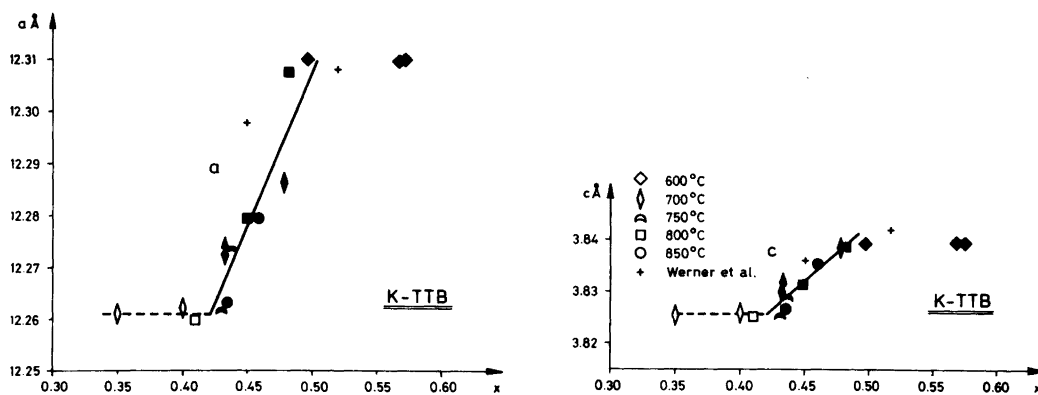


Fig. 2. Cell parameters versus potassium content for K-TTB phase. Filled symbols represent single phase samples. Unfilled symbols represent samples containing several phases and the compositions indicated in these cases are not the composition of the TTB phase but the gross compositions.

and Cs) except that a TTB phase is formed with potassium but not with rubidium and cesium.

Tetragonal tungsten bronzes, TTB. Of the alkali metals investigated here only potassium forms a TTB phase. The theoretical upper compositional limit is $x=0.60$, a value reached when all tetragonal and pentagonal tunnels are completely filled with potassium. However, in the present investigation the observed x values never exceeded 0.57, in agreement with Magnéli's results.⁷ The lower limit of the range is close to 0.42. The limit can be obtained from the variation in the lattice parameters (Fig. 2). Samples with gross composition in the range $0.33 \leq x \leq 0.42$ were always mixtures of TTB and HTB. The potassium content at the limit could not be checked by chemical analysis as TTB cannot be separated from HTB by chemical means. From a refinement of the potassium occupancy parameter in the crystal structure of K-TTB Kihlberg and Klug¹¹ found a composition $x=0.371 \pm 0.008$ in the crystal investigated. X-Ray fluorescence analysis of another crystal from the same batch gave $x=0.34 \pm 0.02$. These values are outside the range found in this investigation, but it is to be noted that the preparation conditions were rather different (see below). Kihlberg and Klug used rather short heating times and the limit found in the present investigation is therefore more likely to represent equilibrium conditions.

Phases with $x > 0.48$ could only be prepared by hydrogen reduction of polytungstate (method b) and not by the normal solid state synthesis (method a). Samples with nominal composition $x \geq 0.50$

prepared according to method (a) were always phase mixtures as indicated by the presence of a few weak extra reflections in the diffraction patterns in addition to the TTB lines. The unknown phase could be removed by the usual purification process and the analysis of the remaining TTB consistently gave $x \leq 0.48$. In method (b) the temperature (600 °C) was lower and the reaction time (≈ 40 min) shorter compared with the conditions normally used in method (a). In order to check whether the TTB with $x > 0.48$ is stable at higher temperature, samples prepared by method (b) having $x > 0.48$ were heated at 800 and 850 °C for 2 days. The X-ray patterns obtained were identical to those of the original samples before heat treatment. The potassium content was also analysed and found to have the same value both before and after heat treatment indicating stability at temperatures up to 850 °C. Réau *et al.*¹⁴ prepared TTB phases with compositions up to $x=0.59$ at 750 °C by the normal solid state synthesis. However, they did not report any analysis and apparently considered the bronzes to have the same composition as the starting mixtures.

At 900 °C and above, TTB phases are not stable (see Fig. 1). After treatment at these temperatures, samples having gross compositions $x > 0.35$ were mixtures of mainly HTB, hexatungstate and tritungstate. In addition there were some weak lines, which came from some unidentified, probably reduced, phase. These samples had obviously not reached a state of equilibrium. The same mixtures were obtained when pure TTB was heated at 900 °C or above for few days and thus seem to be

the result of thermal decomposition of TTB. In order to obtain large single crystals Magnéli⁷ and later Kihlberg and Klug¹¹ prepared TTB by heating for 15–20 min at temperatures between 900 and 1100 °C. The TTB obtained in those experiments was always contaminated by HTB. In the light of the present findings it is likely that the TTB obtained in those experiments was in a metastable or transient state at the higher temperatures.

In Fig. 2 the unit cell parameters of the TTB phase are plotted *versus* x and compared with previously reported values. Both cell parameters are seen to increase up to $x \approx 0.50$ and are then practically constant. This does not mean that $x \approx 0.50$ is the upper limit of composition, however, since the analysis of carefully purified samples gave values up to $x = 0.57$. It is interesting to note that this region of nearly constant lattice parameters is approximately the same as that in which the solid state synthesis does not work. The preparation conditions may thus influence the unit cell parameters. The variation of the cell parameters with respect to potassium content within the linear range ($x = 0.42 - 0.48$) has been refined by the least squares method with the resulting equation $a = (12.006 + 0.605x)$ Å and $c = (3.733 + 0.222x)$ Å [indicated by solid lines in Fig. 2].

Hexagonal tungsten bronzes, HTB. In the potassium, rubidium and cesium systems the HTB phase forms as a single phase in the range $0.19 \leq x \leq 0.33$ for all temperatures investigated (700–950 °C) (see Fig. 1). The upper compositional limit, $x = 1/3$, is reached when all the available alkali sites in the hexagonal tunnels are occupied. Samples with gross composition $x < 0.19$ were not homogeneous HTB phase but mixtures of HTB and other phases (Fig. 1). Chemical analysis of pure HTB phase obtained as single phase, directly or by purification, showed the lower limit to be approximately 0.19. Only about 57% of the available alkali sites are occupied in this case.

In the potassium system, HTB with even lower x values was obtained when samples having a gross composition $x > 0.35$ were heated at 900 °C or above. Low potassium HTB ($x \geq 0.13$) could thus be obtained as one of the products resulting from thermal decomposition of TTB but not by the synthesis method normally employed. Banks and Goldstein¹⁰ report on potassium HTB with x as low as 0.13. They prepared their samples in the normal way from W, WO_3 and K_2WO_4 but used a lower temperature (500 °C) and a longer reaction

time (500 h) than generally used here. Attempts were therefore made here to prepare HTB with $x < 0.19$ under these conditions. The product obtained was mainly unreacted WO_3 with a small amount of HTB phase. After purification, there remained too little HTB to allow a reliable analysis. However, one sample was analysed and found to have $x = 0.17$, but this sample still contained a small amount of WO_3 as judged from its X-ray pattern and the x value of the HTB phase should accordingly be somewhat higher. The range of x observed in the present investigation agrees fairly well, however, with that reported by Réau *et al.*¹⁴ for K ($0.22 \leq x \leq 0.31$) and Wanlass and Sienko¹⁵ for Rb ($0.20 \leq x \leq 0.33$). No corresponding study of the Cs system has been made previously.

The unit cell parameters of some of the $M_x\text{WO}_3$ are presented graphically *versus* composition in Fig. 3. Some previously reported values are included for comparison. The parameters obtained for rubidium and cesium are seen to vary rather smoothly with x but the values for potassium scatter considerably, in particular the c parameter. The a value remains practically constant with x while the length of the c -axis in general seems to increase with x . Values for samples with nearly the same x -value prepared at different temperatures are seen to differ but no systematic variation is obvious. Although the values obtained by Werner *et al.*¹⁶ for one composition are in good agreement with the present data the results reported by Banks and Goldstein¹⁰ are rather different. These authors found an almost smooth increase in both a and c with x (see Fig. 3) and the c values are considerably higher than observed here. Moreover, the samples prepared at the same temperature as that used by Banks and Goldstein (500 °C) give c values which deviate most from their values. Similar variations in the lattice parameters for K-HTB have been observed in a study of the oxidation-reduction transformation between K-HTB and corresponding tungstate.¹⁷ This could then lead to the suspicion that the differences are due to slight variations in the oxygen content of the samples. In order to check this, some samples were prepared deliberately understoichiometric in oxygen. These would then be expected to have extreme lattice parameters. This was not the case, however, as seen in Fig. 3. Oxidizing treatment with *aqua regia* and subsequent heating in air at 200 °C was also performed with some samples but did not change the lattice parameters significantly. The reason for this scattering and

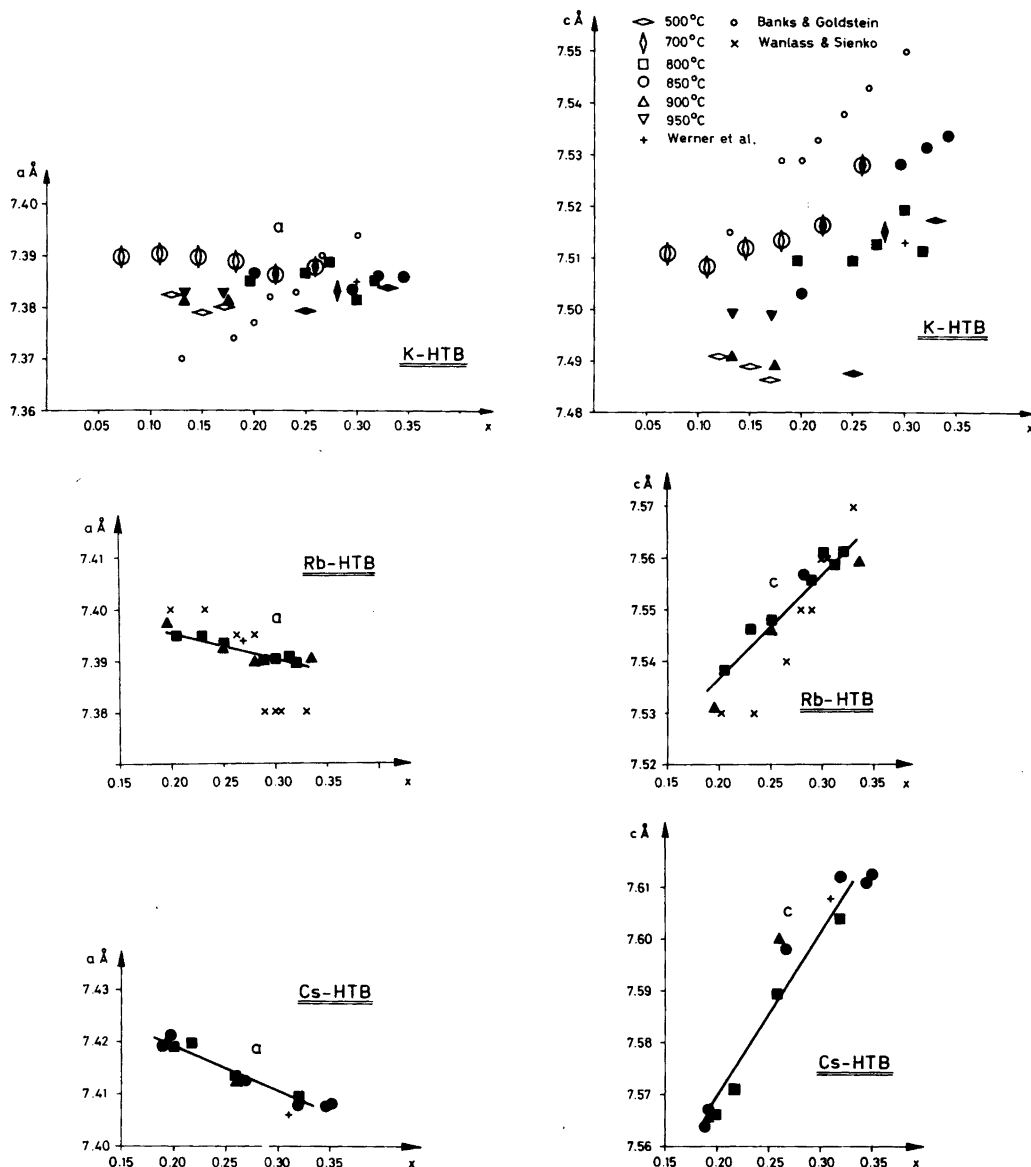


Fig. 3. Lattice parameters versus alkali metal content of potassium, rubidium and cesium HTB. Encircled symbols represent the samples being understoichiometric in oxygen in the gross initial compositions. Filled and large unfilled symbols have the same meaning as in Fig. 2.

disagreement is thus still obscure but may be due to some structural feature not yet detected, for example partial ordering of potassium ions, which is sensitive to the preparation conditions and which influences the lattice parameters.

In contrast to the above behaviour the cell

parameters observed for Rb- and Cs-HTB scatter very little and vary smoothly with x . With increasing x the length of the a axis decreases slightly and that of the c axis increases. The rate of change is almost twice as large for Cs than for Rb. The same trend has been observed by Wanlass and Sienko,¹⁶ but

the absolute values of the cell parameters are slightly different (Fig. 3). As seen in Fig. 3, it is possible that the cell parameters for both Rb- and Cs-HTB are constant for x values above 0.30 but the scattering is too large to allow a definite conclusion about this. The following equations were obtained for the least squares lines fitted to the points in the linear ranges, namely for Rb $a=(7.406-0.050x)$ Å, $c=(7.497+0.202x)$ Å and for Cs $a=(7.436-0.085x)$ Å, $c=(7.507+0.314x)$ Å.

Intergrowth tungsten bronzes, ITB. Optical microscope examination and the X-ray powder patterns revealed that samples of gross composition $0.06 \leq x \leq 0.10$ contained only ITB phases. The purified ITB crystals from various batches were analysed and the alkali metal content was found to be in the range $0.06 \leq x \leq 0.10$. The reproducibility in the analyses was not as good as for the other phases, however, which may be due to the fact that the ITB bronzes formed were always mixtures of different members and never obtained as true single phases. In the potassium system a mixture of ITB and HTB was obtained in the range $0.11 \leq x \leq 0.18$ (see Fig. 1). Rubidium and cesium gave a mixture of HTB and WO_3 in the same range. This anomalous behaviour seems to indicate that the samples had not reached an equilibrium state. In order to check whether equilibrium had been reached in these cases, some samples within this range of these two systems were reground and reheated at 850 °C for one week. The X-ray patterns of the samples were almost the same as before but a few ITB crystals were seen under the optical microscope in several cases. After 2 months, a considerable amount of ITB had formed even if the starting materials were HTB and WO_3 and were kept at separate places in the reaction tube. This indicates that chemical vapour transport must take place. It is thus evident that also for Rb and Cs the stable phases in this region are ITB and HTB but the HTB phase once formed reacts rather slowly with WO_3 .

The temperature is rather critical for the formation of ITB phases. The lower limit is close to 800 °C as samples prepared at this temperature sometimes contained ITB, sometimes only HTB and WO_3 . The ITB phases were obtained up to 950 °C, the upper limit of temperature used in this investigation. The variations of the cell parameters with composition of the ITB phases could not be studied because true single phases were not obtained.

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