

Hexagonal tungsten bronze synthesized from potassium peroxo-polytungstate and its electrical properties

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Peroxo-polytungstic acid, formed by the direct reaction of metallic tungsten with hydrogen peroxide, precipitated an amorphous salt with potassium bromide. Decomposing the precipitate at 400–800°C in air yielded white hexagonal potassium tungstate, $K_xWO_{3+x/2}$ ($x=0.3$), with lattice parameters of $a=7.31$ and $c=7.65$ Å. On the other hand, thermal decomposition in a reducing atmosphere (H_2/H_2O) at 500°C gave dark blue hexagonal tungsten bronze (HTB), K_xWO_3 , with $a=7.38$ and $c=7.52$ Å, which were almost identical to those reported for HTB. It was found that the redox reaction between tungstate and HTB was completely reversible. A porous pellet of the present HTB showed metallic conductivity (≈ 10 S/cm, at 25°C) under dry conditions. In a wet atmosphere with only slight humidity, however, its conductivity was dramatically reduced. The conductivity was recovered by treating it again in a dry condition.

1. Introduction

Tungsten- or molybdenum-based compound with the framework structures attract much attention in relation to intercalation chemistry, which provides the basis for a variety of application fields, for example, secondary batteries, electrochromic devices, etc. In this connection, new synthetic routes for compounds in this class have extensively been investigated [1–3].

Recently we have reported [4] that various tungstates with a defective hexagonal or pyrochlore-type framework, both the which are built out of six-membered rings of corner-sharing WO_6 octahedra, can be obtained by thermal decomposition of an amorphous salt precipitated by reacting peroxo-polytungstic acid (IPA) with a solution of alkaline (or alkaline earth) halide (or nitrate). As those compounds were synthesized in oxidizing atmosphere, they are fully oxidized tungstates such as $K_xWO_{3+x/2}$ (hexagonal, $x \approx 1/3$) and their framework may be lacunar ($K_yW_{1-y/6}O_3$).

The purpose of this investigation is to reveal how the structure and electronic properties of potassium

tungstates thus synthesized change on reduction. It is expected that reduced tungsten compounds show remarkable electronic conductivity due to mixed valence states. We report here comparison between a hexagonal product and conventional potassium hexagonal tungsten bronzes (denoted as K-HTBs), and reversible redox reactions between the reduced and oxidized hexagonal phase obtained from K-IPA. In addition, we show very humidity-sensitive conductivity of reduced hexagonal phase found particularly in the present reduced hexagonal phase at relatively low temperature.

2. Synthetic procedure

Peroxo-polytungstic acid was prepared according to the previously reported method [5]. Metallic W powder was dissolved in 15% H_2O_2 to yield a pale yellow acidic solution. It was then dried at room temperature after removing excess H_2O_2 catalytically with a platinized Pt net, resulting in a yellow glassy substance (IPA) with an approximate empirical formula of $2WO_3 \cdot H_2O_2 \cdot 2H_2O$.

White amorphous substance was precipitated by adding 50 ml of an IPA solution (1.2 mol/l as to

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Table 1

Compounds derived from amorphous precursor (K-IPA). HTB= hexagonal tungsten bronze (K_xWO_3 , $x=0.3$); TTB= tetragonal tungsten bronze (K_xWO_3 , $x=0.57$); HPT= hexagonal tungstate ($K_xW_{1-x/6}O_3$, $x=0.3$).

Heating conditions	(N ₂ balance)	Products
500°C	air	HPT
	H ₂ 10%	HTB
	H ₂ 100%	HTB
700°C	air	HPT
	H ₂ 10%	HTB+TTB+W
	H ₂ 10%, H ₂ O 2%	HTB+TTB
	H ₂ 100%, H ₂ O 2%	TTB+W
800°C	H ₂ O 2%	HPT
	H ₂ 10%, H ₂ O 2%	HTB+TTB
	H ₂ 98%, H ₂ O 2%	K ₂ WO ₄ +W

tungsten) into 50 ml of a stirred KBr solution (1.2 mol/l). After storage for 24 h at 20°C, the precipitate was filtered, rinsed with water and then dried at 70°C. Potassium peroxo-polytungstate (K-IPA) thus formed, a precursor, was decomposed under various conditions as shown in table 1, to give a variety of potassium tungsten oxides. Decomposing it in air yielded pale yellow hexagonal K-tungstate (HPT, $K_xWO_{3+x/2}$ where $x=0.30$ analytically) in a fully oxidized state at temperature ranging from 400 to 800°C. The structure of HPT similarly synthesized at 700°C has been refined and reported by the present authors [6]. On heating K-IPA in reducing atmospheres (H₂ or H₂/H₂O), the product at 500°C was dark blue matter, the hexagonal cell parameters which agreed substantially with those reported for HTBs. A mixture phase of HTB and red-violet TTB (tetragonal tungsten bronze) was formed at a higher temperature in similar reducing atmospheres. The lattice parameters of the compounds formed from K-IPA are compared with those reported in table 2.

3. Structural study

Powder XRD pattern taken with fully oxidized tungstate, $K_xWO_{3+x/2}$ ($x=0.30$), is shown in fig. 1a, where weak but obvious peaks due to a four-fold superstructure in the *a-b* plane (indicated by (▼)) are observed. Such a superlattice has been reported

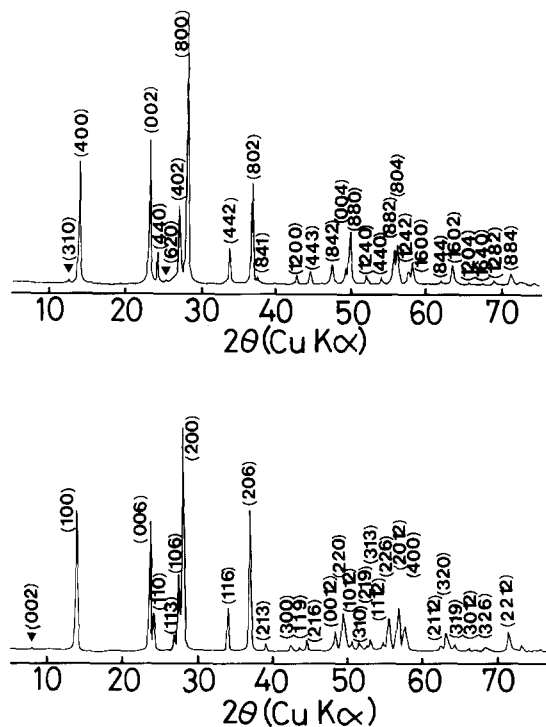


Fig. 1. (a) Powder XRD patterns of oxidized form (HPT); (b) powder XRD patterns of reduced form (HTB).

Table 2
Lattice parameters of HTBs.

x (in K_xWO_3)	x (Å)	c (Å)	Ref.
0.33	7.385	7.534	[9]
0.26	7.385	7.530	[11]
0.32	7.3835(3)	7.5007(4)	[13]
0.20	7.3869(3)	7.5101(3)	
0.30	7.3809(1)	7.5168(1)	this work

by Klug et al. [7] for "potassium hexatungstate" prepared by oxidizing K-HTB ($x=K/W=1/3$) at about 900°C, and, more previously, by Deschavernes et al. [8] for HPT from solid state reaction between K_2WO_4 and WO_3 . Therefore, the present tungstate may be identical to these ones, though its synthetic temperature is remarkably lower. The origin of the superstructure has not been fully understood.

Moreover, the position of excess oxygens in the tungstate is still controversial. Hussain et al. [9] have

suggested that such oxygens are located in the tunnels of the hexagonal framework (fig. 2) together with the potassium atoms. However, this model is unlikely for the present tungstate with $x=0.30$, because its tunnels are almost fully occupied by large K ions and the spacing between K-K is as short as $\sim 1 \text{ \AA}$. It is, thus, reasonable to assume a W-vacancy model, i.e., $K_xW_{1-y/6}O_3$ where $y=6x/(6+x)$. A relatively strong shoulder band at 950 cm^{-1} seen in its IR spectrum (fig. 3a) is assignable to $W=O$ (terminal) and indicates a lacunar W sublattice. Such defective structures have been reported for Cs-tungstates with the pyrochlore-type [10] and hexagonal frameworks [11].

Powder XRD pattern recorded with reduced sample prepared in H_2 at 500°C is shown in fig. 1b. The

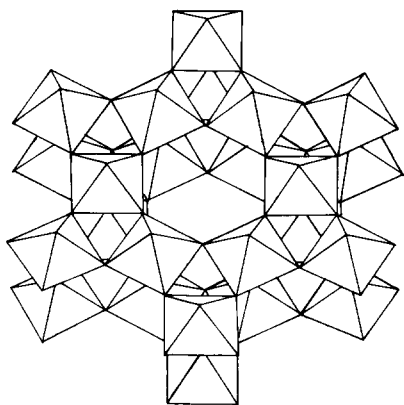


Fig. 2. Hexagonal framework. Octahedra corresponds to WO_6 . Potassium ions are located in the tunnel.

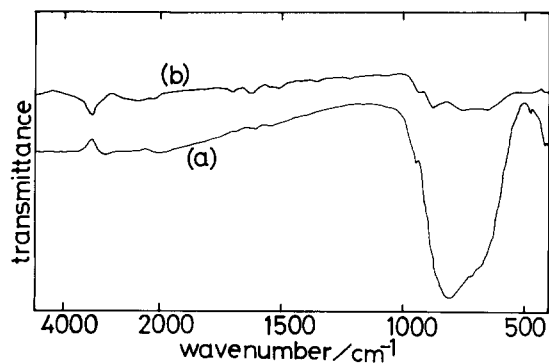


Fig. 3. IR spectrum of HPT and HTB: (a) HPT (oxidized form); (b) HTB (reduced form).

relatively strong $hkl(l=2n+1)$ -peaks characteristic for HTB are observed. No $h0l(l=2n+1)$ -peak is found, but this fact does not exclude the possibility that the compound belongs to the space group $P6_322$, on which Pye et al. [12] argued the structure of $K_{0.26}WO_3$, because such reflections might only be detected by the neutron diffraction. A special structural feature of this compound is that very weak peaks due to a three-fold superstructure along the c -axis (indicated by \blacktriangledown) are often found together with weakened four-fold superlines of the same ones in oxidized tungstate. Krause [13] noted that K_xWO_3 has the incommensurate superlattice row in the c direction with a periodicity of 50 to 250 \AA or more, depending on the composition or synthesizing temperature. However, the periodicity of the present case is much shorter ($3c=22.6 \text{ \AA}$). We have not succeeded in direct observation of such superstructures. A typical lattice image taken with our sample is shown in fig. 4, indicating the lattice is not defective. Contrary to the TEM observation, the infra-red

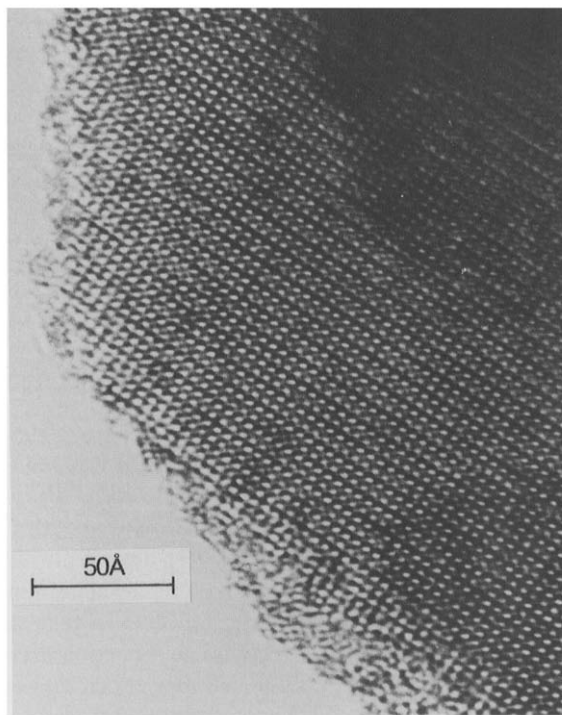
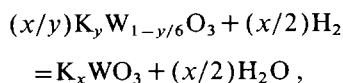


Fig. 4. Lattice image [110] of K_xWO_3 (HTB) synthesized from K-IPA.

spectrum in fig. 3b has a considerably strong band at 950 cm^{-1} due to terminal oxygen ($\text{W}=\text{O}$), indicating that a significant amount of W-vacancies exist in the present HTB. It is thus thought that defects are not populated near the surface of particles. TEM which is usually employed for local analysis can only observe the thin part of a particle and cannot detect the defects at the inner part of a particle.

4. Reduction and oxidation

On heating tungstate ($x=\text{K}/\text{W}=0.30$) in H_2 at 500°C , it was changed into dark blue matter that showed essentially the same XRD pattern as that of HTB (fig. 1b), though the superlattice lines were not always found. The density measurements before and after this process were performed by the gas displacement method using a Shimadzu multivolume pycnometer 1350. The density of the initial tungstate was 6.31 g cm^{-3} which almost agreed with the theoretical one, 6.41 g cm^{-3} , calculated assuming a W-vacancy model, $\text{K}_y\text{W}_{1-y/6}\text{O}_3$ ($y=6x/(6+x)=0.29$, $z=6$). After reduction, the density was increased up to 6.68 g cm^{-3} , which was also comparable with the theoretical value, 6.87 g cm^{-3} , for K_xWO_3 ($z=6$). (The density of $\alpha\text{-Al}_2\text{O}_3$, a standard sample, was 3.92 , as compared with the theoretical 3.99 g cm^{-3} .) These facts again confirm a lacunar tungsten sub-lattice in the tungstate, and indicate its reduction in H_2 takes place according to



where $y=6x/(6+x)$.

Reduction of the tungstate to the HTB was comparatively fast; tungstate peaks completely disappeared from XRD patterns after treatment at 500°C for only one hour. Hussain et al. [9] have reported that similar reduction of tungstate under vacuum or in Ar atmosphere. In their case, however, it takes a long time like three days for complete reduction even at much higher temperature than 850°C . Such a great difference of reaction rates could not simply be accounted for as differences in the P_{O_2} and grain sized ($\leq 1\text{ }\mu\text{m}$ for the former and $10\text{ }\mu\text{m}$ for the latter).

It is, therefore, reasonable to think that the reduction scheme under very low and relatively high P_{O_2} are different.

The fact that reduction in H_2 (or $\text{H}_2/\text{H}_2\text{O}$) rapidly proceeds at relatively low temperature suggests that the activation energies for oxygen transport and concomitant annihilation of W-vacancies (a kind of reconstruction process) are comparatively small. It is interesting, in this connection, to note that, if every seventh (on average) tungsten layer of a tungstate $\text{K}_{6/19}\text{W}_{18/19}\text{O}_3$ (or $\text{K}_{1/3}\text{WO}_{3+1/6}$) is completely vacant and K ions are, instead, inserted there, a lamellar compound to be represented by $\text{K}^+[\text{K}_5\text{W}_{18}\text{O}_{57}]^-$ would be formed. Though such a structure was not found in XRD patterns, it would seem that reduction of the tungstate can rapidly take place utilizing such defective layers partly generated in the compound. A three-fold superstructure along the c -axis found in the present HTB might be accounted for as a reflection of such a reduction scheme.

Re-oxidizing HTB thus formed (or prepared directly from K-IPA in H_2) in air yielded white to pale yellow tungstate as that initially given by K-IPA. Thus redox between HPT and HTB phase is reversible. However, the oxidation process at 500°C was very slow, and required higher temperature (700°C) to complete the reaction within one hour. It is rather natural that oxidation is much slower than reduction, because the former process is generating a considerable number of W-vacancies in an almost complete WO_3 framework and the latter process is eliminating W-vacancies to generate a complete WO_3 framework. The oxidation process from the stable complete framework would need more energy than the reduction from the framework with many defects.

5. Electrical properties of HTB

HTB powder synthesized at 500°C was pressed at $3 \times 10^7 \sim 6 \times 10^8\text{ Pa}$ into a pellet with 2.5 mm in diameter and $2 \sim 3\text{ mm}$ in thickness. After silver electrodes were coated on both faces using silver paste (Tokuriki P-255), this green pellet was heated in H_2 at 500°C for one hour. The final porosity of the sample pellets (calculated from apparent and theoretical density) was in the range of 20–25%. It was visually

confirmed that no interfacial product between the electrodes and HTB was formed. The conductivity was measured by the conventional dc-two probe and ac-two probe techniques.

Immediately after preparation, every sample showed conductivity of about 10 S/cm and its nature was metallic ($d\sigma/dT < 0$). However, their conductivities were dramatically decreased in an usual room atmosphere.

A typical example of such a behavior is shown in fig. 5 as a plot of ρ (resistivity/ Ω cm) versus t (time/min), which seems to be fitted by an empirical function like $\rho = [1/\rho_0 \exp(at) + 1/\rho_1]^{-1}$ where ρ_0, ρ_1 and a are constant and $\rho_0 \ll \rho_1$. We performed the same experiment under a similar conditions using a K-HTB prepared by a conventional method at 850°C, but its resistivity was kept almost unchanged for a long time. This behavior, characteristic of the present K-HTB, may not be associated with an interfacial phenomenon at the electrodes, because the conductivities measured by the dc- and ac-technique agreed very well with each other.

It is reasonable to assume that the resistivity change is caused by atmospheric oxygen or moisture. To check which gas is involved in the phenomenon, similar experiments were carried out in N_2 and dry air with the dew point of -70°C . No substantial resistivity change was observed in both atmospheres, suggesting that moisture was responsible. It was also confirmed that the resistivity was increased in the same way, when the sample put in a $N_2 + 0.5\%H_2O$ atmosphere prepared by bubbling N_2 in a water bath at 0°C . In addition, the resistivity ceased to increase

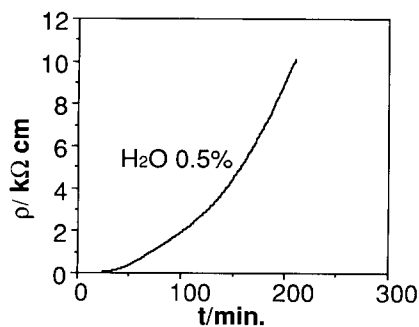


Fig. 5. Resistivity change of HTB in air (20°C , RH 20%, H_2O 0.5%).

when a dry gas was introduced instead of a moist one, as shown in fig. 6.

Weight change of K-HTB powder observed in moist air (or N_2) was rather small, i.e., 0.5% weight gain after storage in an atmosphere with 0.5% H_2O for three hours. Powder sample thus treated under moist air was heated in a He stream and desorbed species were mass-spectroscopically monitored (the TPD measurement). As shown in fig. 7, a TPD spectrum peaked at 140°C is clearly observed for H_2O , while that for O_2 is not distinguishable from background signals. Relatively high desorption temperature of water suggests that it is chemisorbed or intercalated. As the peak is single though broad, water molecules may be bonded with the K-HTB through a single chemical interaction scheme. The infrared spectra of the K-HTB recorded before and after water adsorption are compared in fig. 8. After water adsorption, bands at 950 cm^{-1} probably due to residual $W=O$ become almost missing. This suggests that adsorbed water is bonded to residual $W=O$ by hydrogen bonding. Water adsorption seems to be closely related to a defective structure of the present K-HTB. Observed conductivity decrease is also related to this

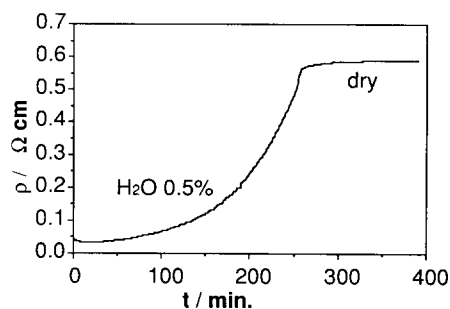


Fig. 6. Resistivity change of HTB in an $N_2 + 0.5\%H_2O$ atmosphere prepared by bubbling N_2 in a water bath at 0°C ($t=0\sim 250$ min.) and in a dry N_2 atmosphere ($t=250$ min. \sim).

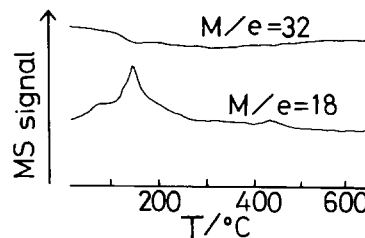


Fig. 7. TPD spectrum of HTB from K-IPA.

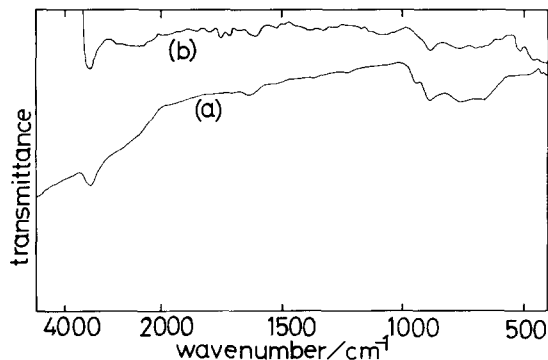


Fig. 8. IR spectra of HTB before and after water adsorption: (a) before water adsorption; (b) after water adsorption (only left in air 20°C RH 30% for four hours).

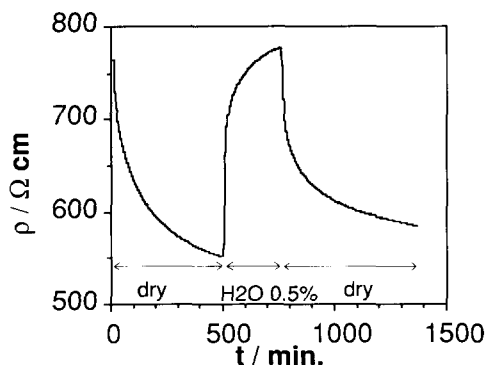


Fig. 9. Resistivity change of a HTB sample of high resistivity with much water in air (20°C, RH 20%, H₂O 0.5%) ($t=0\sim 10$ min.), in dry N₂ ($t=10\sim 500$ min.), in air again ($t=500\sim 760$ min.) and in dry N₂ again ($t=760$ min. ~).

water adsorption. It was also found that the resistivity of the present K-HTB tends to be insensitive to water vapor as heating time in H₂ is prolonged. More studies are needed for details.

It is worth noting that the resistivity change with water becomes reversible depending on conditions. As shown in fig. 6, after only a little water adsorption the resistivity of the sample becomes almost constant when a dry gas is introduced. However, as shown in fig. 9, a sample adsorbing much water and having higher resistivity, decreases its resistivity when a dry gas is introduced. This indicates that part of adsorbed water can be desorbed in dry atmosphere at room temperature, agreeing with a broad TPD spectrum as shown in fig. 7. This phenomenon might

be useful for humidity sensors though the response time with the present sample was too long.

6. Conclusions

On heating K-IPA in reducing atmospheres, hexagonal tungsten bronze is obtained. Redox reaction between tungstate and HTB is reversible. Its mechanism is discussed in connection with W-vacancy model. The electrical conductivity of HTB from K-IPA is decreased in an atmosphere with H₂O and recovered in a dry atmosphere. From IR spectra this is probably due to hydrogen bonding between residual W=O and H₂O. More studies are needed for details.

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