

Humidity sensor using potassium hexagonal tungsten bronze synthesized from peroxo-polytungstic acid

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Received 29 September 1994; accepted in revised form 15 May 1995

Abstract

We have found that potassium hexagonal tungsten bronze synthesized by a new synthetic route at low temperature (500 °C) shows a remarkable increase in resistivity in a humid atmosphere at room temperature. The conductometry performed in various humidities ($P_{\text{H}_2\text{O}} = 2.0 \times 10^{-3}$ –14.6 mmHg) shows that the equilibrium values of resistivity are a clear function of $P_{\text{H}_2\text{O}}$. It is also found that the response time as a humidity sensor is improved from about 5–10 hours to 10–20 minutes by increasing the porosity of the sample pellet from 25 to 35%. The mechanism of resistivity change and the application to a humidity sensor are discussed in this connection.

Keywords: Humidity sensors; Potassium hexagonal tungsten bronze

1. Introduction

In recent years there has been a great deal of interest in the low-temperature synthesis of inorganic materials using precursors [1]. A typical example is the sol–gel technique based on hydrolysis and condensation of metal alkoxide. The formation of a hexagonal form of tungsten trioxide from a hydrothermally prepared precursor ($3\text{WO}_3 \cdot \text{H}_2\text{O}$) is pointed out as an instance close to the present study [2]. Such synthetic routes are advantageous over conventional ones in that they enable us to synthesize various metastable phases because of the lower formation temperature and better compositional uniformity of products. Moreover, special properties can be expected of substances formed at low temperature because defect structures are often different from those of high-temperature formation even though the basic structures are the same. Materials synthesis based on such concepts is called ‘soft chemistry’ or ‘chimie douce’ [3].

We have reported that various tungstates with a defective hexagonal or pyrochlore-type framework can be synthesized through a soft chemical route using precursors precipitated from a peroxo-polytungstic acid (isopoly acid, IPA) solution [4,5]. It has also been shown that tungsten bronze phases with the same framework are formed at relatively low temperature (500–700 °C) by heating such precursors in a reducing atmosphere (10% H_2) [6]. Of these, pyrochlore type Cs_xWO_3 is a new bronze formed for the first time by this low-temperature synthetic process [7].

Potassium hexagonal tungsten bronze (K-HTB, K_xWO_3 ; $x \approx 0.3$) thus formed at 500 °C is not different in basic crystal structure from conventional K-HTB synthesized by well-known solid-state reactions around 1000 °C. Its electrical conductivity is metallic as usual when left in a dry atmosphere after preparation. However, we have found that it shows a remarkable increase in resistivity when it is left in a humid atmosphere at room temperature [6]. This is the first observation of a resistivity increase of inorganic materials by incorporation of water. Infrared spectroscopic observations and density measurements have indicated that this unusual property is probably associated with a special defect structure in the present K-HTB.

The purpose of this paper is to investigate its electrical properties quantitatively in relation to water vapour pressure to demonstrate its applicability to a humidity sensor.

2. Experimental

2.1. Synthetic procedure

Peroxo-polytungstic acid was prepared according to the previously reported method [8]. Metallic tungsten was dissolved in 15% aqueous 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 platinumized platinum net, resulting in a yellow glassy substance (IPA) with the approximate empirical formula $2\text{WO}_3 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$.

A white amorphous substance was precipitated by adding 50 ml of an IPA solution (1.2 mol l^{-1} as tungsten) to 50 ml of a KBr solution (1.2 mol l^{-1}) with stirring. After storage for 24 h at 20°C , the precipitate was filtered, rinsed with water and then dried at 70°C . On heating the thus-formed potassium peroxo-polytungstate in 10% H_2 (N_2 balance) at 500°C for 1 h, dark blue potassium hexagonal tungsten bronze (K-HTB) was obtained.

We prepared conventional K-HTB by the following solid-state reaction for comparison [9]:



Stoichiometric amounts of K_2WO_4 , WO_3 and W were intimately mixed and heated in N_2 at 850°C for 4 h.

2.2. Structural aspects

The powder X-ray diffraction (XRD) profile was taken for the present K-HTB using monochromatized $\text{Cu K}\alpha$ radiation. The 2θ scanning was carried out stepwise with a width of 0.02° and a measuring time of 5 s. In order to diminish a preferred orientation, the sample was well ground and attached softly on a sample holder.

The K/W ratio in this K-HTB (x in K_xWO_3) was determined by chemical analysis. The K-HTB was dissolved in hydrogen peroxide and the concentrations of both K^+ and W^{6+} in the solution were determined by inductively coupled plasma (ICP) emission spectrometry.

2.3. Conductometry

The electrical resistivity was measured by the conventional a.c. two-probe, d.c. four-probe and d.c. two-probe methods.

The d.c. four-probe measurement was carried out as follows. A powder sample of K-HTB was pressed at $6 \times 10^8 \text{ Pa}$ for 8 min into a pellet 11.4 mm in length, 5.3 mm wide and 0.8 mm thick (Fig. 1). After gold electrodes were coated on both sides and at two points on the plane with gold paste (Tokuriki Chemical Corporation No. 8570), this pellet was reheated in 10% H_2 (N_2 balance) at 500°C for 1 h. The final porosity of these sample pellets (calculated from apparent and theoretical densities) was in the range 25–30%. After reheating, its resistivity was measured as a function of $P_{\text{H}_2\text{O}}$. A constant current was made to flow from two outside electrodes with a TR6143 current source (Advantest Corporation) and the electric potential difference between the two inside electrodes induced by the constant current was meas-

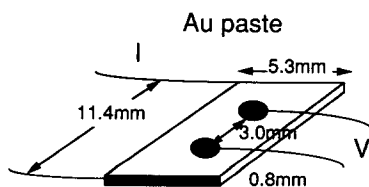


Fig. 1. Schematic view of the sample pellet for the d.c. four-probe measurement.

ured with an HP3457A electrometer (Hewlett-Packard). The electric potential difference for the reverse current direction was also measured in the same way. After confirming that these two values of potential difference were in good agreement, the average of these two values was used to calculate the resistivity. The constant current density employed for this measurement was confirmed to show an ohmic V - I dependence. Thus the electrical properties we report in this paper cannot be associated with interfacial phenomena between the pellet and the electrodes.

The d.c. two-probe measurement was carried out preliminarily using the HP3457A electrometer. We employed two types of sample pellets for the d.c. two-probe measurement in order to investigate how the porosity of the sample pellet affects the resistivity change. One is the same as for the d.c. four-probe measurement (porosity 25–30%) and the other is fabricated as follows. A powder sample of K-HTB was pressed at $3 \times 10^7 \text{ Pa}$ for 1 min into a pellet 2.5 mm in diameter and 2–3 mm thick. After gold electrodes were coated on both sides using gold paste (Tokuriki Chemical Corporation No. 8570), this pellet was reheated in 10% H_2 (N_2 balance) at 500°C for 1 h. The final porosity of these sample pellets was in the range 30–40%.

The a.c. two-probe measurement was also carried out preliminarily on a part of this work using HP4192A apparatus (Hewlett-Packard). The frequency employed for this measurement was 100 Hz, at which the X -value (imaginary part of the impedance) was negligible compared to the R -value (real part of the impedance). Thus the impedance measured in this way is assumed to be identical with the resistance of the d.c. two-probe measurement.

2.4. Gravimetry

Gravimetric analysis was performed using a high-sensitivity balance (Cahn 2000 Recording Electrobalance).

Gravimetry of K-HTB at different $P_{\text{H}_2\text{O}}$ values was carried out at room temperature to investigate the relationship between $P_{\text{H}_2\text{O}}$ and n (in $\text{K}_x\text{WO}_3 \cdot n\text{H}_2\text{O}$).

Thermogravimetry of K-HTB ($\text{K}_x\text{WO}_3 \cdot n\text{H}_2\text{O}$; $n = 0.22$) in dry air ($P_{\text{H}_2\text{O}} = 2.0 \times 10^{-3} \text{ mmHg}$) at a heating rate 1°C min^{-1} was also carried out to investigate the chemical potential of water molecules in K-HTB.

3. Results and discussion

3.1. Structural aspects

The present K-HTB shows a sharp powder XRD profile as shown in Fig. 2, indicating that it has high crystallinity despite the low formation temperature (500°C). This profile was taken with a sample left in a humid atmosphere ($P_{\text{H}_2\text{O}} = 5$ – 15 mmHg) at room temperature for more than a week. Therefore it is estimated to have contained a considerable amount of water and to have turned from metallic to

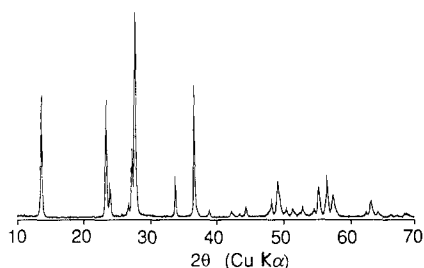


Fig. 2. Powder XRD profile of the K-HTB synthesized by heating potassium peroxo-polytungstate in H_2 at $500^\circ C$.

semiconducting (see Section 3.2). It has been confirmed that a fresh and water-free sample shows almost the same profile except for slight changes in lattice parameters. These fine changes in the crystal structure accompanied by water incorporation are now being investigated to understand the mechanism of the resistivity change.

We performed the Rietveld structural refinement to check how the present K-HTB is different in structural details from the conventional one prepared at higher temperature. There were no distinguishable differences between these K-HTBs, except that distortion of the WO_6 coordination octahedron in the present K-HTB is somewhat greater [10]. Therefore, it may be considered not to be special in the basic structure of the framework. The distorted nature of WO_6 might be related to the fact that tungsten vacancies exist in the K-HTB, which has been confirmed by the presence of an IR band at $960\text{--}980\text{ cm}^{-1}$ due to vibration of $W=O$ [6].

The K/W ratio was determined as 0.3 from ICP analysis, which is not significantly different compared with that of the conventional K-HTB formed by the solid-state reaction.

3.2. Incorporation of water into K-HTB

A fresh water-free sintered sample pellet of the present K-HTB showed a metallic resistivity as low as $0.1\ \Omega\text{ cm}$ at room temperature in a dry atmosphere. However, its resistivity was dramatically increased in a wet atmosphere (Fig. 3). The saturated value of resistivity reached $200\text{--}800\ \Omega\text{ cm}$ depending on the water-vapour pressure (P_{H_2O}) of the atmosphere. At the same time, a significant amount of water incorporation by the sample pellet was gravimetrically observed. The water content n in $K_xWO_3 \cdot nH_2O$ in equilibrium with $P_{H_2O} = 12\text{ mmHg}$ was about 0.2.

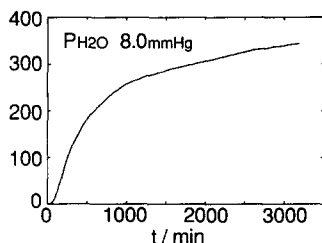


Fig. 3. Resistivity change of K-HTB in a humid atmosphere, $P_{H_2O} = 8.0\text{ mmHg}$ (a.c. two-probe measurement).

It was found that samples with relatively low water content (and therefore low resistivity) only ceased to increase in resistivity when a dry gas (dew point $-70^\circ C$, $P_{H_2O} = 2.0 \times 10^{-3}\text{ mmHg}$) was introduced instead of a humid one (Fig. 4). On the other hand, those with high water content (therefore, high resistivity) reduced their resistivity reversibly (Fig. 5). Such behaviour can be accounted for by assuming that the P_{H_2O} in equilibrium with $K_xWO_3 \cdot nH_2O$ is given by a function of n schematically illustrated in Fig. 6, in which $\ln P_{H_2O}$ is related to the chemical potential (μ) of the water molecule in the K_xWO_3 phase by

$$\ln P_{H_2O} = (\mu - \mu^0) / (kT) \quad (2)$$

where μ^0 is the μ in equilibrium with the standard P_{H_2O} ($= 760\text{ mmHg}$). Let us assume, for simplicity that the μ is represented by a familiar form,

$$\mu = E + RT \ln[\theta / (1 - \theta)] \quad (3)$$

where E is the internal energy associated with water adsorption or intercalation at a set of sites in K_xWO_3 , and θ the occupancy of the sites (i.e., $\theta = n/n^*$, n^* being the number of sites per mole). If there is only one kind of site and E does

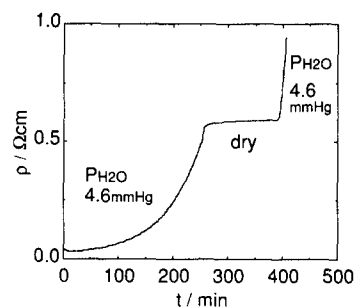


Fig. 4. Resistivity change of K-HTB when a dry gas was introduced at the initial stage of water incorporation (a.c. two-probe measurement).

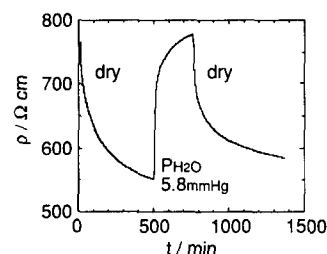


Fig. 5. Resistivity change of K-HTB when a dry gas was introduced at the saturated stage of water incorporation (a.c. two-probe measurement).

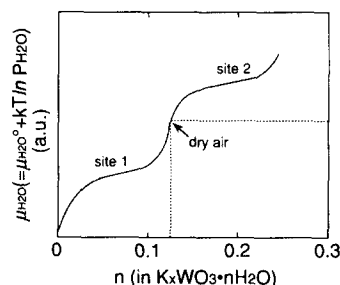


Fig. 6. Schematic expression of P_{H_2O} vs. n in $K_xWO_3 \cdot nH_2O$.

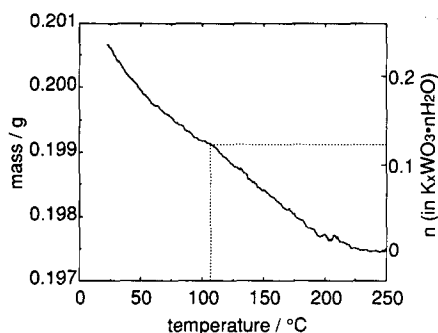


Fig. 7. Water-desorption curve for the present K-HTB with water content $n = 0.22$ in dry air ($P_{\text{H}_2\text{O}} = 2 \times 10^{-3}$ mmHg) at a heating rate of 1°C min^{-1} .

not depend on n , the relationship of Eq. (2) is reduced to the Langmuir isotherm. On the other hand, a function in Fig. 6 can be derived by postulating that the K-HTB phase has two kinds of water-adsorption sites (sites 1 and 2), the internal energies of which are far separated from each other (i.e., $E_2 - E_1 \gg RT$). In order to confirm the function in Fig. 6, water desorption from $\text{K}_x\text{WO}_3 \cdot n\text{H}_2\text{O}$ ($n = 0.22$) was investigated thermogravimetrically in dry air ($P_{\text{H}_2\text{O}} = 2.0 \times 10^{-3}$ mmHg). As shown in Fig. 7, the desorption curve has a kink at about 110°C , indicating that phenomena at lower and higher temperatures are different in nature. Water loss at the lower-temperature region is due to its desorption from site 2 at a higher energy level because the equilibrium value of n in this atmosphere at 20°C was determined experimentally as about 0.15. Accordingly, the curve in the higher-temperature region represents the desorption from site 1 at a lower energy level, and can be fitted satisfactorily by the theoretical n - T relationship under equilibrium. E_1 is estimated to be -50 to -40 kJ mol^{-1} from this fitting. E_2 is estimated to be about -10 kJ mol^{-1} because the water incorporation into site 2 is reversible in the $P_{\text{H}_2\text{O}}$ range 5–15 mmHg at room temperature. Details of the $P_{\text{H}_2\text{O}}$ - n isotherm are under investigation, and will be published together with discussion on the mechanism of water incorporation.

3.3. Resistivity change by incorporation of water

It is evident from the above discussion that, in sensing humidity in a usual environment, the adsorption and desorption processes of water are involved with site 2. Therefore, we investigated the applicability to a humidity sensor as follows. After reheating the sample pellet under the same condition as that for the synthesis, a wet gas ($P_{\text{H}_2\text{O}} = 20$ mmHg) was introduced. The resistivity in equilibrium with $P_{\text{H}_2\text{O}} = 20$ mmHg at 25°C (RH 84%) reached about $600 \Omega \text{ cm}$. At this stage a dry gas (dew point -70°C , $P_{\text{H}_2\text{O}} = 2.0 \times 10^{-3}$ mmHg) was introduced to the sample. Then, a new equilibrium for this $P_{\text{H}_2\text{O}}$ was attained at a resistivity of about $250 \Omega \text{ cm}$, which corresponds to the water content $n = 0.15$. From this equilibrium state, the resistivity increase was observed in response to stepwise increases in $P_{\text{H}_2\text{O}}$. As shown in Fig. 8, clear equilibrium values of the resistivity were observed

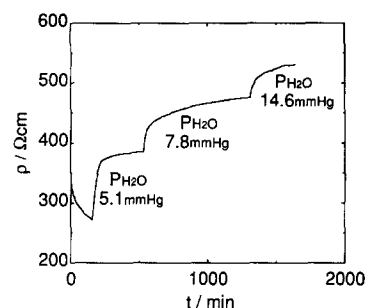


Fig. 8. Resistivity change of K-HTB at room temperature when $P_{\text{H}_2\text{O}}$ was increased stepwise (d.c. four-probe measurement).

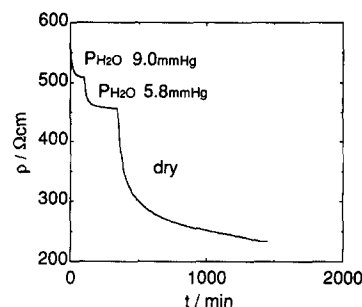
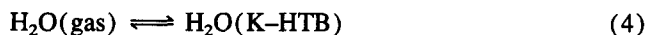


Fig. 9. Resistivity change of K-HTB at room temperature when $P_{\text{H}_2\text{O}}$ was decreased stepwise (d.c. four-probe measurement).

for each value of $P_{\text{H}_2\text{O}}$. For stepwise decreases in $P_{\text{H}_2\text{O}}$, its resistivity decreased as shown in Fig. 9, indicating good reversibility of the process expressed by



These results, which were performed by the d.c. four-probe method using a sample pellet with a relative density of 75%, demonstrate the applicability of the present K-HTB to a humidity sensor. The response time using this pellet was about 5–10 h, which is too slow for practical use. In order to improve the response time, we formed sample pellets with a higher porosity of 35% (relative density 65%) and measured their resistivity by the d.c. two-probe method. As shown in Fig. 10, the response time was much improved to about 10–20 min. This means that the response time is controlled by the bulk diffusion of water in the sample pellet. Therefore, much faster response can be expected by forming K-HTB into a thin film.

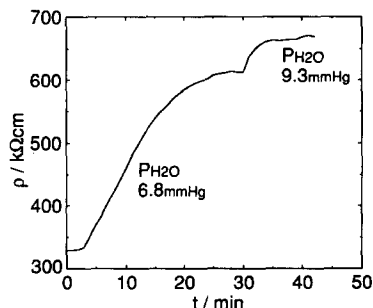


Fig. 10. Resistivity change of K-HTB pellet with 35% porosity (d.c. two-probe measurement).

The mechanism of resistivity increase by water incorporation is now being investigated in relation to the defect structure. Since tungsten complex oxides with hydrated water or with a layer structure are reported in the literature, we are proposing a model based on a layer structure. Briefly, the present K-HTB has a layer structure and the electrical path is separated by intercalation of water between the layers. More studies are needed for details.

Acknowledgement

This work was supported by a Grant-in Aid for Scientific Research from the Japanese Minister of Education, Science and Culture (04205024).

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