

Short Communication

Synthesis and Characterization of Vanadium Substituted Potassium Tungsten Bronzes, $K_xV_yW_{1-y}O_3$

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Received 24 December 2011, accepted in revised form 26 March 2012

Abstract

A series of vanadium substituted potassium hexagonal tungsten bronzes $K_xV_yW_{1-y}O_3$ (K-HTB) were prepared by conventional solid state method at 800 °C with compositions of $x = 0.30$ and $0.00 \leq y \leq 0.15$. A mixture of K-HTB and non bronze phases with $y \geq 0.20$ was observed. The proportion of this non bronze phase increases with increasing vanadium content. The non bronze phases in the mixture could not be indexed yet. In contrast, a very small amount of vanadium can be substituted in potassium tetragonal tungsten bronzes (K-TTB) at 800 °C with $x = 0.50$ and $0.00 \leq y \leq 0.02$, however at 700 °C vanadium substituted K-TTB can be prepared with $0.00 \leq y \leq 0.05$. Further substitution of vanadium in K-TTB decomposes to K-HTB and non-bronze phases.

Keywords: Tungsten bronzes; Vanadium substituted bronze; Bronzoids.

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doi: <http://dx.doi.org/10.3329/jsr.v4i2.9349>

J. Sci. Res. 4 (2), 507-514 (2012)

1. Introduction

Tungsten bronzes, M_xWO_3 , are well known non-stoichiometric ternary metal oxides where M is an electropositive metal atom with $0 < x < 1$. The crystal structure of tungsten bronzes [1,2] can be described as corner-sharing WO_6 octahedra, forming various kinds of tunnels where the metal atoms are located. Depending on the size, amount of the interstitial metal atom and synthesis temperature tungsten bronzes adopt four different structure types, namely, Perovskite Tungsten Bronzes (PTB) [3,4], Tetragonal Tungsten Bronzes (TTB) [5], Hexagonal Tungsten Bronzes (HTB) [6] and Intergrowth Tungsten Bronzes (ITB) [7]. Tungsten Bronze have interesting physical and chemical properties for which these materials are very demanding for modern technology [1,2 and references therein].

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Tungsten bronzes may also be written as $M_xW_y^{5+}W_{1-y}^{6+}O_3$ showing the degree of reduction of the bronzes depending on the value of x . The W^{5+} can be partially ($x < y$) or fully ($x = y$) replaced by other pentavalent metal ions of suitable sizes to prepare isostructural phases of partially or fully oxidized bronzes. The isostructural fully oxidized phases are known as bronzoids [8].

The potassium tungsten bronzes are known to form TTB, HTB and ITB at ambient pressure [1]. Fig. 1 shows the crystal structure of the HTB that contains hexagonal and trigonal tunnels along the c -direction. The potassium atoms occupy specific sites, the hexagonal tunnels.

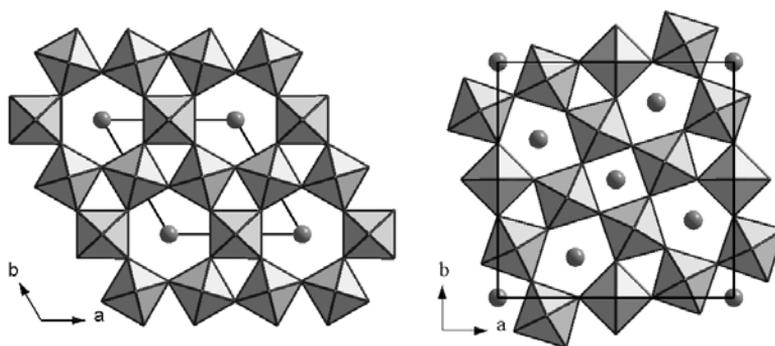


Fig. 1. Structural model of hexagonal tungsten bronze, HTB (left) and tetragonal tungsten bronze, TTB (right).

The homogeneity range of alkali metal K-, Rb-, and Cs-HTB phases were reported for $0.19 < x < 0.33$ [6]. The lower stability limit greatly depends on the preparation conditions and can be extended up to $x = 0.15$ [1]. The upper stability limit corresponds to the full occupancy of the hexagonal tunnels, that is, $x = 0.33$.

The structure of K-TTB consists of a framework of corner sharing WO_6 octahedra, with tunnels of trigonal, square, and pentagonal running along the short crystallographic c -axis (Fig.1). The pentagonal and to some extent the tetragonal tunnels are occupied by K atoms. The compositional range of K-TTB was reported for $x = 0.42 - 0.57$ [1], however, K-TTB with $x > 0.48$ could only be prepared by reduction of an appropriate polytungstate mixture with hydrogen gas at about 600 °C. Notably, the K-TTB phases were reported to be stable up to 850 °C [9].

The electrical and optical properties of HTB phases were intensively studied [10–12], and recently the x -dependent superconductivity has been investigated [13–15]. It was also reported that Nb substituted alkali metal HTB showed interesting optical and electrical properties [16]. Literature survey shows that there are reports on niobium and tantalum substituted alkali metal tungsten bronzes [17–24] and almost no report on vanadium substituted bronzes.

Vanadium, compare to its neighbor in the periodic table, shows wide range of oxidation states and coordination polyhedral for which it offers a versatile oxide chemistry. Bergström *et al.* [25] showed how the distorted octahedra changed into regular octahedra during lithium intercalation into a V_6O_{13} framework. The simultaneous change in coordination polyhedral and the oxidation state is an essential requirement of multiple charge / discharge process in rechargeable batteries. As such, the variety of vanadium oxidation state and their redox process readily allow the insertion and or removal of ions without destroying the framework. It was, therefore felt necessary to conduct a systematic study of vanadium substitution in tungsten bronzes to see the amount of vanadium that can accommodate in the parent structure. Herein, we report a new series of compounds in the system $K_xV_yW_{1-y}O_3$.

2. Experimental

A series of $K_xV_yW_{1-y}O_3$ compounds for $0.00 \leq y \leq 0.30$, $x = 0.30$ and $0.00 \leq y \leq 0.20$ when $x = 0.50$ were prepared in evacuated sealed silica tube by conventional solid state methods according to the following equations:



All the reactants, WO_3 (99.998 %), WO_2 (99.9 %), V_2O_5 (99.9985 %), except K_2WO_4 (99.5%), were from Alfa Aesar. K_2WO_4 was prepared according to Eq. (1) the reaction (1) by heating overnight at 600 °C. Both WO_3 and V_2O_5 were heated in air overnight at 500 °C in porcelain crucible before use. The purity of all the reactants was checked by using X-ray powder diffraction.

The reactants with appropriate molar ratio (Eqs. (2) and (3)) were mixed mechanically in an agate mortar for about half one hour to make homogeneous intimate mixture, and then transferred into cleaned, preheated (800 °C) silica tubes. The tubes were then evacuated ($\sim 10^{-2}$ torr) at room temperature for two hours and sealed under vacuum. The sealed tubes were heated in a muffle furnace at temperature 800 °C and 700 °C for seven days. The products were cooled slowly to room temperature by taking it off from the furnace.

All products were characterized by optical microscope. The X-ray powder diffraction patterns were taken using a Guinier-Hägg focusing camera, $CuK\alpha_1$ radiation and Si ($a = 5.43088 \text{ \AA}$) as an internal standard. The X-ray films were evaluated with a computerized LS 20 line film scanner using the software SCANPI [26]. The d-values and the lattice parameters were then refined by using program PIRUM [27]. To cross check the X-ray results obtained by Guinier-Hägg focusing camera, the X-ray powder patterns of few samples were also recorded by a Bruker diffractometer. The preparation conditions of the bronzes and the results of lattice constants are given in Table 1.

Table 1. Preparation conditions and results of unit cell parameter refinement. All samples were prepared at 800 °C except those marked with “#” which were prepared at 700 °C.

Nominal composition $K_xV_yW_{1-y}O_3$	Observed color	Observed phase(s)	Unit cell parameter (Å)		
			<i>a</i>	<i>c</i>	
<i>x</i> = 0.30	<i>y</i> = 0.00	Blue	HTB	7.3817(3)	7.5310(7)
	<i>y</i> = 0.02	Blue	HTB	7.3772(2)	7.5225(3)
	<i>y</i> = 0.05	Blue	HTB	7.3614(6)	7.505(1)
	<i>y</i> = 0.08	Blue	HTB	7.3380(8)	7.533(1)
	<i>y</i> = 0.10	Blackish blue	HTB	7.312(1)	7.557(2)
	<i>y</i> = 0.15	Blackish blue	HTB	7.243(1)	7.691(3)
	<i>y</i> = 0.20	Brownish	HTB + u	7.245(1)*	7.714(2)*
	<i>y</i> = 0.25	Brownish	HTB + u	7.269(2)*	7.720(5)*
	<i>y</i> = 0.30	Brown	HTB + u	7.261(1)*	7.724(1)*
<i>x</i> = 0.50 [#]	<i>y</i> = 0.00	Reddish violet	TTB	12.2709(9)	3.8296(4)
	<i>y</i> = 0.02	Reddish violet	TTB	12.2669(8)	3.8280(3)
	<i>y</i> = 0.05	Reddish violet	TTB	12.2666(5)	3.8272(2)
	<i>y</i> = 0.08	Reddish black	TTB + HTB + u	nr	nr
	<i>y</i> = 0.10	Dark blue	TTB + HTB + u	nr	nr
	<i>y</i> = 0.15	Dark blue	HTB + u	nr	nr
<i>x</i> = 0.50	<i>y</i> = 0.00	Reddish violet	TTB	12.2589(4)	3.8256(2)
	<i>y</i> = 0.02	Reddish violet	TTB	12.2619(6)	3.8252(2)
	<i>y</i> = 0.05	Reddish blue	TTB + HTB + u	nr	nr
	<i>y</i> = 0.08	Blackish blue	HTB + u	nr	nr
	<i>y</i> = 0.10	Blackish blue	HTB + u	nr	nr
	<i>y</i> = 0.15	Blackish blue	HTB + u	nr	nr

* cell parameters of HTB phase only; nr = not refined; u = few reflections of unidentified phase. Numbers in parentheses are standard deviation in the last digits.

2. Results and Discussion

The X-Ray powder patterns shows that $K_{0.30}V_yW_{1-y}O_3$ prepared at 800 °C possesses single phase of HTB for $y \leq 0.15$ as seen in Fig. 2. On further substitution of vanadium ($y > 0.15$), a mixture of HTB and unknown phase appeared, which could not be identified as known bronze phases. Only HTB reflections were used for samples with vanadium $y > 0.15$ to refine the cell parameter of the HTB phases.

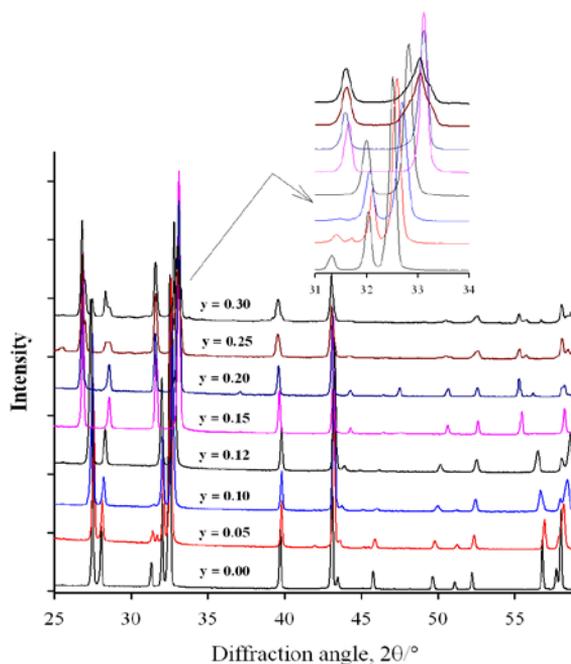


Fig. 2. X-ray diffraction patterns of some selected samples with nominal compositions $K_{0.3}V_yW_{1-y}O_3$. An enlarge view (inset) shows that the number of diffraction peaks for certain planes are systematically decreasing with increasing V content. The patterns are shifted vertically for the sake of clarity.

With increasing vanadium content ($y > 0.15$) the relative peak intensities of the HTB phase gradually decreased, whereas the peak intensities of the unknown phase increased with $y \geq 0.20$. The successive incorporation of V^{5+} in $K_{0.30}V_yW_{1-y}O_3$ was clearly supported by the change of the cell parameters; the results are listed in Table 1 and presented in Fig. 3.

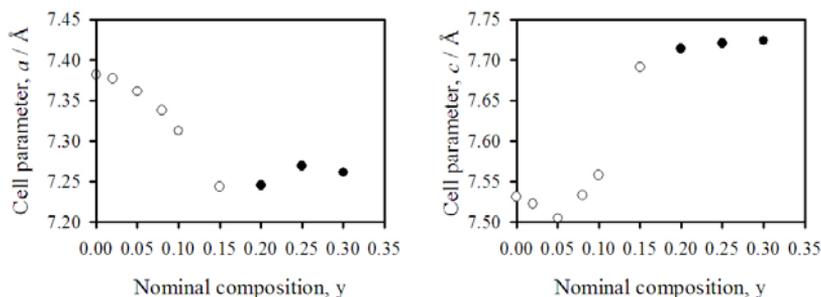


Fig. 3. Variation of cell parameter (a and c) of $K_{0.30}V_yW_{1-y}O_3$ with nominal vanadium content, y . The solid circles represent that the samples with these nominal compositions were a mixture of two phases. Only HTB phases were considered for the refinement of cell parameters.

Cell parameter refinement of HTB system shows a systematic variation with vanadium content (y) though the data are a bit scattered. There is clear trend of decrease in a up to $y = 0.15$ whereas c up to $y = 0.05$. However, the cell parameter c increases up to $y = 0.15$ and then both cell parameter almost constant with $y \geq 0.15$ (see Fig. 3). The decrease in both of the cell parameters can be comparable with the previously reported Nb substituted Rb- and Cs-HTB [16]. However, the reason for increase in cell parameter c needs further investigations.

Tungsten bronzes are reduced oxides which could be oxidized to polytungstate, $M_xWO_{3+x/2}$. This transformation is closely related to the change of the lattice constants. Hussain *et. al.* [28] found that the lattice parameter a decreased (7.39 to 7.32 Å) whereas c increased (7.51 to 7.63 Å) from HTB to polytungstate. In Nb doped K-HTB Hussain *et. al.* [16] reported that both the cell parameters (a and c) decreased with increasing niobium content. With such analogy, in this present investigation, the systematic variation of lattice parameters with increasing vanadium content support that partially oxidized bronzes might have formed. The decrease in unit cell volume for $K_{0.50}V_yW_{1-y}O_3$ may be due to the fact the ionic size vanadium ion V^{5+} is smaller than that of W^{5+} .

The $K_{0.50}V_yW_{1-y}O_3$ prepared at 800 °C (for 7 days) showed TTB phase when $y \leq 0.02$. The homogeneity range was widen up to $y = 0.05$ when samples were prepared at 700 °C. Pure K-TTB phase was stable up to 850 °C; at 900 °C it decomposed mainly to HTB, hexatungstate and tritungstate [9]. The present study shows that the stability and homogeneity range of vanadium substituted potassium tetragonal tungsten bronzes favors more at lower temperature (700 °C) than higher temperature (800 °C). Further substitution of vanadium (y up to 0.15) in this composition formed mixture of TTB and HTB phases along with some unknown phased (extra lines, Fig. 4). The weak lines could not be identified as any known phase of bronzes.

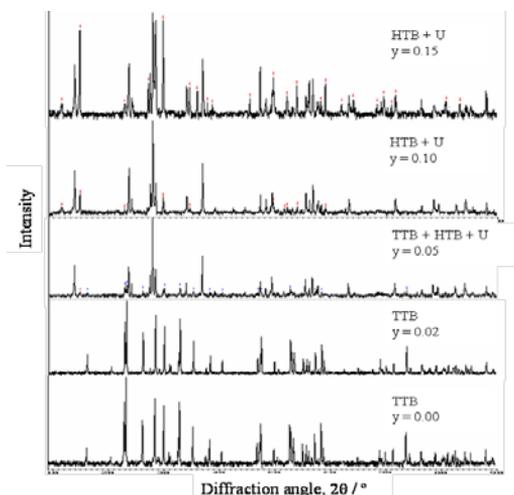


Fig. 4. X-ray powder pattern of the sample of nominal composition: $K_{0.50}V_{0.05}W_{0.95}O_3 + Si$, Reaction temperature: 800°C, Unindexed line for unknown phase (U) is indicated by red mark. Regular face lines are indexed as HTB phase. Blue mark indicates TTB Phase.

Lattice parameters (a and c) of the samples $K_{0.50}V_yW_{1-y}O_3$ prepared at 700 °C showed, though little, a gradual decrease with increasing vanadium content up to $y = 0.05$. Cell parameters observed for $K_{0.50}V_yW_{1-y}O_3$ prepared at 700 °C is little bit larger than those of the samples prepared at 800 °C. This variation in cell parameters may depend on preparation temperature as it was reported that the stability and homogeneity ranges of tungsten bronzes depend on preparation conditions [1].

Acknowledgments

The authors are grateful to the Ministry of Science and Information & Communication Technology, Government of Bangladesh and Alexander von Humboldt Foundation, Germany, for financial supports.

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