

Facile synthesis and structure characterization of hexagonal tungsten bronzes crystals



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ABSTRACT

A facile molten-salt route was used to synthesize hexagonal $\text{Cs}_{0.33}\text{WO}_3$, $\text{Rb}_{0.33}\text{WO}_3$ and $\text{K}_{0.30}\text{WO}_3$ crystals. The three isostructural compounds were successfully prepared from the reaction of MxWO_3 powders ($\text{M} = \text{Cs, Rb, K}$) in the CsCl/NaCl , RbCl/NaCl and KCl/NaCl fluxes, respectively. The structure determination and refinement, based on single-crystal X-ray diffraction data, are in agreement with previous works, possessing space group $\text{P6}_3/\text{mcm}$. The a and c parameters vary non-linearly with increasing radii of the M^+ cations (r_{M}) that is coordinated to twelve oxygen atoms. Both the volumes of unit-cell and WO_6 octahedra vary linearly with r_{M} , which become smaller from $\text{Cs}_{0.33}\text{WO}_3$ to $\text{K}_{0.30}\text{WO}_3$. The distortion of WO_6 octahedra as well as isotropic displacement parameters increases from $\text{Cs}_{0.33}\text{WO}_3$ to $\text{K}_{0.30}\text{WO}_3$. The geometry of the WO_6 octahedron becomes more regular with increasing r_{M} . These structural trends arise from the effective size of the M^+ cation.

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1. Introduction

The oxygen deficiency in tungsten oxides results in a complex-ordered structure known as the Magneli structure, while the ternary addition of the cation leads to the tungsten bronze structure. The tungsten bronzes (MxWO_3) are typical example of non-stoichiometric compounds, in which M is a univalent metal and x lies between 0 and 1 [1,2]. They crystallize in a number of different phases and represent an unusually interesting series with properties ranging from metallic to semiconducting depending on the univalent metal M [3]. There are four structurally different tungsten bronze phases namely, perovskite tungsten bronze (PTB), hexagonal tungsten bronze (HTB), tetragonal tungsten bronze (TTB) and intergrowth tungsten bronze (ITB) [3,4]. The crystal structure of sodium tungsten bronzes is of PTB and HTB. Tetragonal Na_xWO_3 for $x = 0.25$ as well as 0.35 are identified, and cubic Na_xWO_3 for x values from 0.45 to 0.85 [5]. The Na_xWO_3 film crystallized with the hexagonal symmetry of space group $\text{P6}/\text{mmm}$ have also been reported [6]. Another three alkali-HTB compounds, Cs_xWO_3 , Rb_xWO_3 and K_xWO_3 have been found with a space group of $\text{P6}_3/\text{mcm}$ or P6_322 . It was revealed that the x value is limited to 0.33 at maximum to maintain the hexagonal phase for these three compounds [1,4,7]. These three MxWO_3 compounds show interesting electrical properties, such as superconductivity at very low

temperatures for $0.15 < x < 0.33$. The superconducting transition temperature T_c ranges between 1 and 7 K and increases gradually towards lower x values [3]. Furthermore, the hexagonal MxWO_3 phase is also regarded as being highly attractive in solar filter applications, because the absorption is small enough in the visible range but is strong in near infrared (NIR) lights [8]. The NIR absorption increases with increasing x value of MxWO_3 has been reported in the literatures [1,9,10].

The alkali-HTB phase was first reported by Magneli and Blomberg in 1951 [11]. Later, Magneli found that the unit cell dimensions of the tungsten bronzes were approximately the same irrespectively of the alkali metal atoms being potassium, rubidium or cesium [12]. He carried out the first single-crystal X-ray diffraction study on a tiny $\text{Rb}_{0.27}\text{WO}_3$ crystal and indicated that the crystal structure was determined to possess a hexagonal symmetry with a space group of $\text{P6}_3/\text{mcm}$ [9]. However, there have been several crystal-structure determinations of three compounds since the original model proposed by Magneli. The space group of either $\text{P6}_3/\text{mcm}$ or P6_322 has been reported in few cases [13–17].

In order to solve the structural discrepancy as described above, we need to prepare alkali-HTB samples. The traditional methods for preparing the hexagonal tungsten bronze by the reactions of various oxide materials at higher temperatures in reducing atmospheres have been reported [1,7,18]. These preparations mostly give polycrystalline material or the quality of crystals not good enough to study their structural characteristics. Compared with powder diffraction data, more accurate structural details can be

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obtained by single crystal X-ray diffraction (SCXRD) data. Therefore, two crystal synthesis techniques, fused salt electrolysis as well as chemical transport method, have already been reported in the literatures. The crystal growth of tungsten bronzes by fused salt electrolysis was first reported by Scheibler in 1860 [19]. As far as we know, only non-hexagonal Na_xWO_3 and tetragonal K_xWO_3 crystals have been grown by fused salt electrolysis with predictable compositions [19,20]. Intergrown clusters of different crystalline phases often occurred without using a seed crystal. Growing crystals of alkali metal hexagonal tungsten bronzes (HTB) and tetragonal tungsten bronzes (TTB) have also been made by chemical transport in a temperature gradient. However, extremely toxic materials, such as HgCl_2 , HgBr_2 , HgI_2 , and Cl_2 , were employed as transport agents in the synthesis route [21,22]. In order to synthesize the alkali-HTB crystals with quality good enough for SCXRD, we have developed a new safe and easy route via molten-salt method in the present study.

The crystal structures of isostructural $\text{Cs}_{0.33}\text{WO}_3$, $\text{Rb}_{0.33}\text{WO}_3$ and $\text{K}_{0.30}\text{WO}_3$ were determined using as-grown crystals in the study. One of the main structural features in the hexagonal $\text{Cs}_{0.33}\text{WO}_3$, $\text{Rb}_{0.33}\text{WO}_3$ and $\text{K}_{0.30}\text{WO}_3$ is the existence of the six-membered WO_6 octahedral rings running parallel to the c axis, as shown in Fig. 1. The top and bottom vertices of the octahedral pyramids in each WO_6 octahedron are O1 oxygen atoms. Others are four oxygen atoms (O2), coplanar with one W atom in each WO_6 octahedron. The rings interconnected by sharing one of WO_6 octahedra exhibit a layered, planar structure parallel to (0001). Within the ring, two of O2 atoms in each WO_6 group are shared by adjacent WO_6 groups on either side. Each layer is linked by O1 atoms to form a three-dimensional framework. The alkali element (M) such as Cs, Rb and K are accommodated in the broad channels and lie midway between two six-membered WO_6 octahedra rings. Each M atom is coordinated with 12 oxygen atoms (O2) forming a hexagonal prism. Since the M^+ cations have different effective radii, systematic variation in the geometry of the WO_6 and MO_{12} groups is expected. One of the purposes of this study is to examine the structural trends as well as the influence of alkali metals on the stability for alkali-HTB compounds. Using SCXRD analysis, this study shows that the geometry of the WO_6 groups varies in a systematic and expected manner.

2. Experimental procedures

The polycrystalline samples of Cs_xWO_3 , Rb_xWO_3 and K_xWO_3 were first synthesized using a high-temperature solid-state reaction technique with high-purity (AR grade) ingredients: Cs_2CO_3 ,

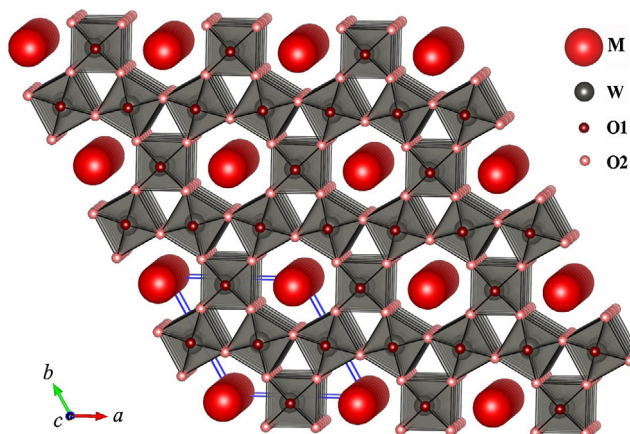


Fig. 1. Crystal structure of $\text{Cs}_{0.33}\text{WO}_3$ framework projected on a - b planes.

Rb_2CO_3 , K_2CO_3 and H_2WO_4 (Sigma-Aldrich Co.). These reactants with appropriate molar ratio in wet (de-ionized water) medium were heated and mixed by a magnetic stirrer with a hotplate for several hours. The mixed material was calcined at an optimized temperature at 700 °C for 5 h in alumina crucible in a reducing atmosphere in the presence of carbon black. All the resulting powders of tungsten bronzes exhibit a deep blue color. The phase compositions of these samples were determined by X-ray diffraction analysis (XRD, Shimadzu XRD-6000) using the $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The absorption properties of these three samples were investigated by using a Jasco V670 UV-Vis-NIR spectrophotometer. In order to produce single crystals via molten-salt method, these synthetic tungsten bronze powders were then combined with the salt fluxes of CsCl/NaCl , RbCl/NaCl and KCl/NaCl , respectively. These mixtures were ground and then dried at 120 °C for 1 day. These initial substances were sealed into evacuated silica ampoules and annealed at higher temperatures. The growth process was finished by cooling the ampoules in air. Synthesized tungsten bronze crystals were released from flux by washing with deionized water. Elemental analysis was performed on the synthetic crystals with an energy dispersive X-ray spectrometer (EDX, Oxford INCA 350X-act) attached to a JEOL JSM-6390 scanning electron microscope. EDX and structural refinement of SCXRD data revealed the average chemical composition of as-grown crystals. Crystals of each product were mounted on glass fibers for diffraction. The as-grown crystals of these three compounds was selected for SCXRD intensity data collection at room temperature using a Bruker AXS SMART CCD diffractometer equipped with Mo radiation ($\lambda = 0.71073 \text{ \AA}$). Processing of the data was accomplished with the use of the program SAINT; an absorption correction was applied to the data using the SADABS program [23]. The unit cell dimensions were determined by a least-squares fit of collected reflections. The crystal structure was analyzed and refined with a full-matrix least-squares method of the Bruker SHELXTAL Version 5.1 software package. The crystallographic data of our three as-grown crystals are summarized in Table 1. Table 2 also presents their atom coordinates and isotropic displacement coefficients. Raman measurements were performed by using a microscopic Raman system (RAMaker, Protrustech Co., Ltd., Taiwan). An exciting line of 532 nm was supplied by a diode laser (CNI) with a power of 12 mW. The exposure time was 10 s with 10 accumulations. Calibration was done using a silicon standard where the band is generally observed at 520 cm^{-1} . The corresponding spectral resolution was in the range of 1 cm^{-1} .

3. Results and discussion

3.1. Sample preparations

Fig. 2 exhibits the typical XRD patterns of the synthesized Cs_xWO_3 , Rb_xWO_3 and K_xWO_3 powders annealed at 700 °C for

Table 1

Unit cell constants and data-collection parameters of three flux-grown HTB specimens.

Chemical formula	$\text{Cs}_{0.33}\text{WO}_3$	$\text{Rb}_{0.33}\text{WO}_3$	$\text{K}_{0.30}\text{WO}_3$
Space group	$\text{P6}_3/\text{mcm}$	$\text{P6}_3/\text{mcm}$	$\text{P6}_3/\text{mcm}$
a (Å)	7.4035(2)	7.3842(3)	7.3742(5)
c (Å)	7.6144(2)	7.5682(3)	7.5169(5)
Cell volume (\AA^3)	361.4(1)	357.4(1)	354.0(1)
Density (calc.)	7.612	7.258	6.859
Absorption coeff. (mm^{-1})	52.607	54.951	49.180
Reflections collected	4743	3954	4099
R_1 (%) ($I > 2\sigma(I)$)	1.70	1.70	3.01
R_1 (%) (all data)	1.98	1.70	3.01
Largest $\Delta e/\text{\AA}^3$	2.10/−2.98	1.22/−1.96	2.91/−2.97

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