Supercritical carbon dioxide assisted growth of sodium tungsten bronze (Na_xWO_3) crystallites

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The tungsten bronzes, with general formula M_xWO_3 ($0<x<1$, M = electropositive metals such as alkali or alkaline earth metals), have been extensively studied for their interesting chemical, electrical, and optical properties and potential technical applications in superconductivity [1], secondary batteries [2], large scale static reflective displays, and ion selective electrodes [3, 4], etc.

Since the compound of Na_xWO_3 was first prepared by Wohler in 1823 [5], various synthetic technologies have been developed to prepare tungsten oxide bronze: the conventional Straumanis method (high temperature reduction of Na_2WO_4, WO_3 by metallic W) [6]; the electrochemical reduction of tungstate [7]; solvothermal [8] and the mechanochemical synthesis [9].

Recently, cubic diamonds and large size magnesium carbonate single crystals were grown in molten sodium and supercritical carbon dioxide hot system in our group [10, 11]. These crystal growth phenomena in supercritical systems have not been elucidated sufficiently despite their importance and are of much interest since they may be more complex than those in liquid or vapor phases. Herein, we report that sodium tungsten bronze crystallites can be grown under the conditions of sodium and supercritical carbon dioxide system by adding the metallic tungsten powder.

A 12 ml high temperature stainless steel autoclave was employed. In a typical run, 2.3 g of metallic sodium (98% purity) after removing the protecting solvent, 1.2 g of metallic tungsten powder (99% purity) with the average diameter of 2 μm and 10.0 g of dry ice (>99% purity) were put in the autoclave, respectively. The sealed autoclave was placed in a furnace, heated to 600 °C at a rate of 10 °C/min and stayed for 20 hr, then opened after it was cooled down to ambient temperature. It was observed with naked eyes that there existed orange red bulks on the surface of solid product. They were collected by hand picking and then washed with hot distilled water for several times and dried at 110 °C. The final product weighted 0.3 g.

The X-ray diffraction patterns of the products were recorded using Philips Xpert Pro (Cu K_α=1.5418 Å) in the 2θ range from 20° to 80°. The morphology of the sample was observed on a scanning electron microscope (SEM) (Hitachi X650). A LABRAM-HR confocal laser micro-Raman spectrometer was employed to characterize the products, performed at ambient temperature using the 514.3 nm line of Ar ion laser as the excitation source.

Powder X-ray diffraction was performed to determine the phases of the crystal samples. The diffraction patterns of a powder sample crushed from the prepared orange solid grown at 600 °C were shown in Fig. 1. All the sharp reflections of XRD pattern could be indexed to cubic phase sodium tungsten bronze Na_xWO_3 with x=0.58, compatible with literature value (PDF JCPDF 750238). As the sample is not readily soluble in acid condition, the precise Na content could not be estimated by atomic absorption spectroscope or inductively coupled plasma (ICP) analysis. But the Na content in cubic tungsten bronze could be calculated from the experimentally observed lattice parameter a_0 Å using Vegard relationship: $a_0=3.7845+0.0821x$ Å [12]. The yielded x value is about 0.59. In addition, the crystalline bronzes Na_xWO_3 were found to exhibit aesthetically interesting colors ranging from deep blue to red to yellow as the value of x increased from 0.25 to 0.46 to 0.7 [13]. In our experiments, the obtained crystals show in orange red color.

Fig. 2a shows SEM image of the prepared crystal grains. Many small crystal grains can be clearly seen and the crystallites in the sample appear to be distinctive cuboid shape with the diameter of several microns and different lateral length. Since the SEM sample has been crushed for XRD analysis, the face of fracture along the lateral direction can be clearly observed, indicating the as-prepared Na_xWO_3 is brittle and the original sample should be in high aspect ratio which is well consistent with the previous reports [14]. Fig. 2b is the enlarged SEM picture of a typical crystal grain in Fig. 2a, the crystal with cubic shape and a smooth, flat surface can be observed clearly and the size of the crystal is about 4 μm. Under the optical microscope, these crystallites appear in bright orange red color, easily identified even with the naked eye.

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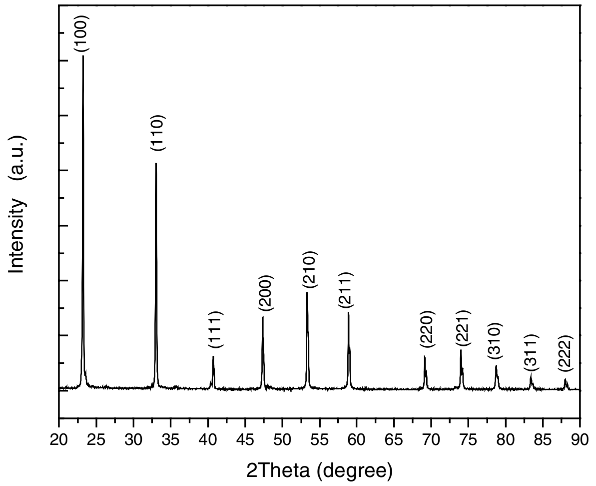

Figure 1 The X-ray diffraction pattern of a powder sample crushed from crystals grown at 600 °C.

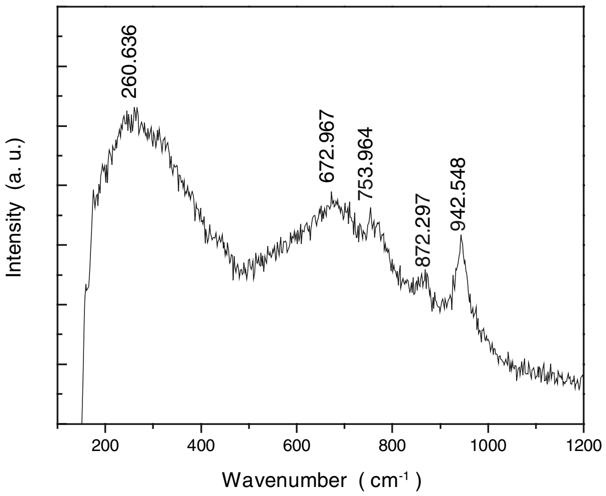

Figure 2 Raman spectrum of sodium tungsten bronze sample.

Micro Raman spectroscope was used to character the crystals of sodium tungsten bronze (Fig. 3). They were recorded with 30 s time constant in order to insure the observed features were not luminescence. The structural arrangements of tungsten bronze compounds provide empty tunnel where ion can be accommodated. As the concentration of inserted ion increases, distortion from ideal ReO_3 structure tends to appear. For example, when sodium ion is inserted, different Na_xWO_3 compositions are formed, firstly monoclinic, then orthorhombic, afterwards tetragonal and final cubic, as x increases from 0 to 0.9 [15]. Raman analysis is a powerful tool to characterize the tungsten bronzes with different structures. As shown in Fig. 3, in low frequent region, the broad and strong peak centered at 260 cm^{-1}, which is usually observed in cubic phase tungsten bronzes, can be regarded as the result of the typical distorted WO_3 lattice. In addition, no peaks at 340 cm^{-1} were observed, suggesting there are no pure WO_3 existed in our samples. The three peaks at 753, 872, and 942 cm^{-1} in higher frequent region can be attributed to the stretching mode of terminal W=O bands and the stretching and bending mode of W–O–W bands [16]. The sharp peak at 942 cm^{-1} indicates the sample is well crystalline, according to the reports of Sweedler *et al.* [17]. At present, we cannot explain the presence of the broad peak centered at 672 cm^{-1}. It might be that the deviation from stoichiometric distribution of Na ion in the lattice contributes to line width of some mode more than others.

In our sealed reaction system, the CO_2 is in a supercritical state (31 °C, 73 atm) and our previous research suggested that it can be reduced by metallic sodium at the temperature higher than 350 °C and the main products were carbon and sodium carbonate. After this reaction, the system pressure was still high for the amount of CO_2 was in excessive for oxidation of sodium [10]. For those metallic tungsten powder exposed to supercritical carbon dioxide, they could be oxidized mainly to tungsten trioxide (WO_3) and low oxidized state tungsten oxides such as WO_2, $W_{17}O_{49}$ etc. Indeed, we carried out blank

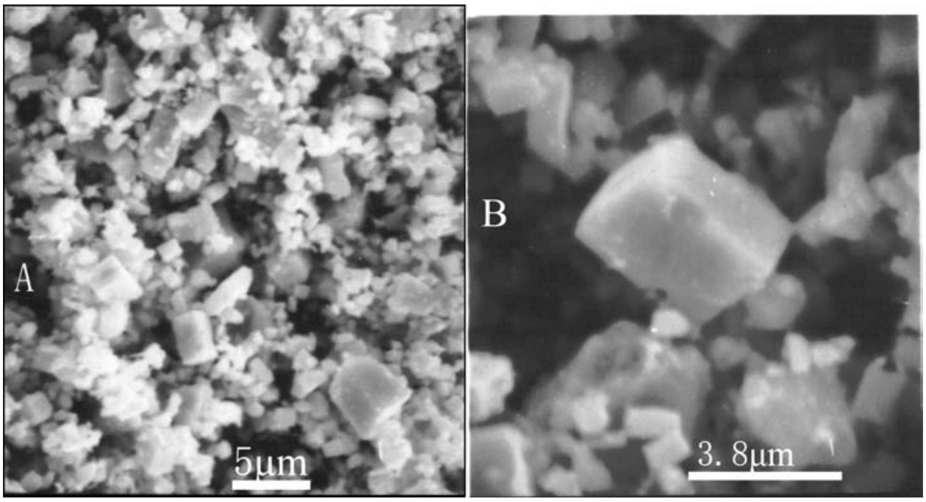

Figure 3 (a) SEM image of the sodium tungsten bronze crystallites. (b) SEM image of a typical sodium tungsten bronze crystallite.

experiment by heating pure tungsten powder in the high pressure supercritical carbon dioxide at 600 °C and found these tungsten oxide compounds. Due to the relative high vapor pressure of these tungsten oxides, they will have significant presence in the gas-phase [18]. When these tungsten oxides were deposited on the surface of the sodium carbonate, they would transform to sodium tungstate and sodium ditungstate. The melting point of pure sodium tungstate is about 700 °C and the eutectic point of Na_2WO_4–$Na_2W_2O_7$ is 622 °C, respectively [19]. At our reaction temperature, these sodium tungstates should be in a molten state, that is, become a liquid. When the rest of tungsten oxides dissolved in the liquid, the phase of tungsten bronzes can be formed. On the condition that the liquid is saturated by tungsten bronzes, the crystals of sodium tungsten bronzes would nucleate and grow. Most of sodium tungstates are easily soluble in water, while sodium tungsten bronze is hard to dissolve in water. So, no sodium tungstates residues can be detected in XRD measurement. The possible chemical reactions are expressed as follows (Scheme 1). It also should be noted that the possibility of forming sodium tungsten bronze in traditional Straumanis mechanism was ruled out in our case, for there was no co-existence of Na_xWO_3 and impure of metallic W that was always presented in Straumanis method [6]. In addition, the Na_xWO_3 product should be distributed homogenously in Straumanis route, but, most of Na_xWO_3 presented in the surface of solid products by our method.

In order to examine the effects of the reaction atmosphere, temperature and pressure, and reactants on the growth of crystallites of sodium tungsten bronze, a series of relevant experiments were carried out by altering the experimental conditions of the processes. Heating the mixture of sodium and tungsten in the air at 600 °C, the product was not sodium tungsten bronze but tungsten and sodium carbonate, which suggested that the production of sodium tungsten bronze is dependence on the supercritical carbon dioxide atmosphere. As the reaction was conducted at 500 °C, the solid products were graphite, sodium carbonate and tungsten, no sodium tungsten bronze could be detected. When the reaction temperature were maintained at 600 °C, increasing the amount of reactant sodium or decreasing the amount of reactant carbon dioxide will result in the decrease of system pressure, only little sodium tungsten bronze crystals can be obtained. It is also found that increasing the amount of carbon dioxide is in favor of the conversion from tungsten to sodium tungsten bronze which indicated the growth of crystallites of sodium tungsten bronze is sensitive to the reaction temperature and system pressure. Since sodium tungsten bronze crystal has many possible structures at different sodium content, we varied the ratio of reactants of tungsten and sodium, but all the tungsten bronze products were found to have cubic phase with nearly the same sodium content. This result can be explained by the fact that the cubic phase sodium tungsten bronze is the thermodynamic stable phase at this reaction temperature and atmosphere.

$$4Na + 3CO_2(Sc) \longrightarrow 2Na_2CO_3 + C_{(graphite)}$$

$$2W + 3CO_2 \longrightarrow 2WO_3 + 3C$$

$$WO_3 + Na_2CO_3 \longrightarrow Na_2WO_4 + CO_2$$

$$(2\text{-}x)WO_3 + xNa_2WO_4 \longrightarrow 2Na_xWO_3 + (x/2)O_2$$

$$WO_3 + Na_2WO_4 \longrightarrow Na_2W_2O_7$$

Scheme 1 The typical chemical reactions in our experiment.

The above studies illustrate a method to grow cubic sodium tungsten bronze (Na_xWO_3) crystallites in supercritical CO_2 system using metallic sodium and tungsten as starting materials. The reaction temperature and the system pressure of CO_2 are crucial parameters for the formation of these crystallites. At 600 °C, the produced crystallites are cube-like and in diameter of several microns. It is proposed that these crystallites are nucleated and grown in the liquid of sodium tungstates which are derived from the combination of the sublimated tungsten oxides and sodium carbonate at the interface of gas and solid phase. This method may be applied to grow other bronze compounds also.

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