Low-temperature Atmosphere-free Molten Salt Synthesis of NIR-shielding CsₓWO₃

Can Li, a Litao Kang, ab Yuting Zhu, a Qingjuan Wang, a Xiaolin Zhao, ab Hongwei He, a Dangxin Tian, c and Jianjun Liu b

a Laboratory of Green Energy Materials and Storage Systems, College of Materials Science and Engineering, Taiyuan University of Technology, Taiyuan 030024, P. R. China

b State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201899, P. R. China

c Hebei Tianbo Construction Science and Technology Co., LTD., Baoding 071051, P. R. China

* Corresponding Author. Email: kanglxty@163.com (L.T. Kang); jliu@mail.sic.ac.cn (J.J. Liu)

Received October 25, 2017; Revised November 22, 2017

Citation: C. Li, L. Kang, Y. Zhu, Q. Wang, X. Zhao, H. He, D. Tian, and J. Liu, Nano Adv., 2017, 2, 47–52.

With LiCl-KCl molten salt as reaction medium, caesium tungsten bronze (CsₓWO₃) with high visible transparency and decent NIR (near infrared) shielding ability was synthesized from CsOH-H₂O, H₂WO₄, and W. Experimental results indicated that the molten salt not only enhanced mass transport of the CsₓWO₃ formation reaction, but also protected CsₓWO₃ from air oxidation. These merits enabled us to prepare CsₓWO₃ at a relatively low temperature of 400 °C in air. The as-obtained CsₓWO₃ delivered both high visible transmittance (54%) and high NIR shielding ability (94%). On the contrary, the solid state reaction product adopted a (CsₓO)₀.₄ₓ₋₀.₃ₓW₂O₅ phase with no detectable NIR shielding ability. This method may also be applicable to synthesize other low-valence materials that are unstable in air at high temperatures.

KEYWORDS: Molten salt synthesis; CsₓWO₃; Near infrared shielding; Caesium tungsten bronze

I. Introduction

Tungsten bronze involves a series of non-stoichiometric compounds with a chemical formula of MₓWO₃, where M stands for inserted cations such as NH₄⁺,¹ 1 alkali ions,² ³–⁶ etc. In MₓWO₃ system, both W⁵⁺ (dark blue) and W⁶⁺ (pale yellow) exist,⁷ ⁸ and their ratio could be easily regulated by external stimuli, resulting in a dramatic transparence variation. Therefore, MₓWO₃ is widely studied in electrochromic,⁹ gasochromic,¹⁰ and photochromic¹¹ devices. Besides applications as optically-dynamic devices, MₓWO₃ shows a relatively wide band gap of 2.62 eV and is transparent for visible light. At the same time, the high-dense free electrons donated by M cations endow this materials an outstanding NIR shielding ability due to the localized surface plasmon resonance and small-polaron absorption.³ ¹² This infrared shielding feature makes MₓWO₃ highly competitive as transparent heat-insulating filter¹³ for window glass and photothermal materials for cancer therapy.¹⁴ In the application of photothermal cancer therapy, MₓWO₃ is injected into tumors in a form of dispersion, and can thermally kill the cancer cells when being irradiated and heated by NIR laser.¹⁴ As a transparent heat-insulating filter, MₓWO₃ can selectively cut off the infrared light in the sunshine to depress indoor solar heat gain, while keeping a clear vision and good natural lighting condition, as showed in the illustration in Figure 1. Therefore, MₓWO₃ coatings on window glasses are expected not only to reduce air-cooling energy consumption, but also to improve living comforts of buildings and automobiles.

In 2007, Takeda and Adachi prepared several MₓWO₃ materials by a solid state reaction in H₂(95%)-N₂(5%)
atmosphere at 800 °C. The excellent NIR shielding ability was achieved in this system after milling, but the high-temperature process and the use of H₂ are energy consuming and potentially dangerous. In 2010, Guo et al. developed a water controlled-release solvothermal method to prepare dispersive Cs₂WO₄ nanorods with excellent NMR shielding ability. In 2014, Wang et al. further prepared (NH₄)₂WO₄ by a hydrothermal method at only 100 °C. However, this method still involves some disadvantages such as low productivity and long reaction time, etc. Therefore, it is still worthy to explore new methods to prepare MₓWO₃.

Significantly, molten salt synthesis (MSS) employs a molten inorganic melts as liquid reaction media, which can accelerate reaction rates and virtually isolate the reactants and products from air. Therefore, this method is highly desirable for the low-temperature and atmosphere-free preparation of oxidizable materials. Depending on the nature of salts, the operational temperature of molten salt synthesis ranges from near 100 to over 1000 °C, allowing the access to a variety of materials, including BaMoO₄, BaWO₄, and CaWO₄. Therefore, molten salt presents a low temperature and atmosphere-free method for the facile preparation of functional materials. In this work, we demonstrate the successful MSS preparation of Cs₂WO₄ at only 400 °C in an ambient atmosphere. Optical measurement revealed that the obtained Cs₂WO₄ delivered a visible transmittance of 53.5% and a NIR shielding ability of 93.6%. In contrast, the solid state reaction (SSR) product showed a Cs₂O₃·4W₂O₈ phase with no detectable NMR shielding ability. This approach may also be applicable to synthesize other metastable materials unstable in air at high temperature.

2. Experimental

2.1 Preparation of Cs₂WO₄

In a typical synthesis process, W powder, CsOH·H₂O, H₂WO₄ (molar ratio: 11/66/189) and LiCl–KCl eutectic mixture (molar ratio: 59/41) were manually ground in a mortar for 10 min. The molar ratio of raw materials and molten salt (sample A) match well with the hexagonal phase Cs₂WO₄ (JCPDS NO.831334, a = b = 7.412 Å, c = 7.598 Å, α = β = 90°, γ = 120°), without any detectable impurity peaks. On striking contrary, the SSR products (sample-B and -C, Figure 2a), regardless of the heating atmosphere, are all composed of cubic phase (Cs₂O₃·4W₂O₈ (JCPDS NO.470566, a = b = c = 10.304 Å, α = β = γ = 90°) and metallic W (JCPDS NO.040806, a = b = c = 3.165 Å, α = β = γ = 90°), suggesting an very incomplete reduction reactions. Figure 2b-c shows the XPS of sample-A and –B. The survey spectra detect the signals of tungsten, oxygen, caesium and carbon. The appearance of carbon should be attributed to surface contamination, which was used as an internal standard (284.5 eV) to calibrate the XPS binding energy. The W4f XPS spectra of sample-A and –B were further analyzed to determine the chemical states of tungsten. For sample-A, both W4f½ and W4f½/2 peaks are asymmetric and could be divided into two doublets, corresponding to W⁵⁺ (W⁴⁺f½ at 34.0 eV, W⁵⁺f½ at 36.1 eV) and W⁶⁺ (W⁶⁺f½ at 35.3 eV, and W⁶⁺f½ at 37.4 eV), respectively. While, the two XPS peaks of sample-B are symmetric and their binding energies (35.2 and 37.3 eV) agree

Research Article

Nano Advances

benefits of molten salt synthesis, a control SSR experiment was also performed in air (sample-B) or N₂ (sample-C) atmosphere, with the same W, CsOH·H₂O, H₂WO₄ ratio and heating protocol but without addition of LiCl–KCl salt.

2.2 Characterization

The phase compositions of the samples were determined by X-ray diffraction (XRD) on a DX-2700 diffractometer (Cu Ka radiation, λ = 0.1542 nm). The surface composition and chemical state of the samples were determined by X-ray photoelectron spectroscopy (XPS) with a Perkin-Elmer PHI 5600 X-ray photoelectron spectroscope using an Al Ka source. The binding energy of the XPS was calibrated by shifting the Cls peak to 284.5 eV. The morphology of samples were analyzed by a JEM-2100F field emission transmission electron microscope (FETEM) and selected area electron diffraction (SAED) images were obtained with an accelerating voltage of 200 kV. The number-based particle size distribution was analyzed by a laser diffraction particle size analyzer (Shimadzu SALD-7000).

Thermal gravimetric analyses (TG) and differential scanning calorimetry (DSC) were recorded on a TGA/DSC 3+ HT/1600 instrument between 30 and 400 °C in N₂ at a heating rate of 10 °C/min. The thickness of the composite film can be controlled by changing casting times (increased by ~ 8 µm for each casting time). Optical properties of the obtained films were monitored on a Hitachi U-4100 UV–vis-NIR spectrophotometer in a wavelength range of 300–2500 nm.

3. Results and discussion

The phase compositions of sample-A, -B and -C were determined by XRD analyses, as shown in Figure 2a. All diffraction peaks of the MSS product (sample-A) match well with the hexagonal phase Cs₂WO₄ (JCPDS NO.831334, a = b = 7.412 Å, c = 7.598 Å, α = β = 90°, γ = 120°), without any detectable impurity peaks. On striking contrary, the SSR products (sample-B and -C, Figure 2a), regardless of the heating atmosphere, are all composed of cubic phase (Cs₂O₃·4W₂O₈ (JCPDS NO.470566, a = b = c = 10.304 Å, α = β = γ = 90°) and metallic W (JCPDS NO.040806, a = b = c = 3.165 Å, α = β = γ = 90°), suggesting an very incomplete reduction reactions. Figure 2b-c shows the XPS of sample-A and –B. The survey spectra detect the signals of tungsten, oxygen, caesium and carbon. The appearance of carbon should be attributed to surface contamination, which was used as an internal standard (284.5 eV) to calibrate the XPS binding energy. The W4f XPS spectra of sample-A and –B were further analyzed to determine the chemical states of tungsten. For sample-A, both W4f½ and W4f½/2 peaks are asymmetric and could be divided into two doublets, corresponding to W⁵⁺ (W⁴⁺f½ at 34.0 eV, W⁵⁺f½ at 36.1 eV) and W⁶⁺ (W⁶⁺f½ at 35.3 eV, and W⁶⁺f½ at 37.4 eV), respectively. While, the two XPS peaks of sample-B are symmetric and their binding energies (35.2 and 37.3 eV) agree.
well with the data of W^{+}. In these spectra, the XPS signal of metal W was not detected, probably because the limited detecting depth of XPS (<2 nm) is thinner than the oxide shell of the metallic W after 400 °C, 2 h annealing in air. In general, the XPS and XRD results all indicate that MSS can effectively promote the formation of Cs_{x}WO_{3} at relative low temperature.

Figure 3a shows the TG-DSC curves of the raw material of sample-A to describe the thermal behavior of this MSS system. A gradual weight loss of ~19 % was observed from room-temperature to 150 °C, accompanied by a broad endothermic peak. This weight loss should be attributed to the release of surface adsorbed water.

Between 150 ~ 220 °C, there are a 12 % weight loss and several sharp endothermic peaks, stemming from the loss of coordination water. Above 220 °C, the weight of the system kept almost unchanged, but a dramatic and symmetric endothermic peak centered at 345 °C was detected. This endothermic peak should be ascribed to the melt process of the employed salt. In fact, the low eutectic melting point of the LiCl-KCl is 353 °C, but after the addition of other components, the real eutectic melting point of the reaction multi-composition system would further drop. Based on the above analyses, a schematic illustration of this MSS process was extracted and displayed in Figure 3b. Firstly, all the raw materials and salts formed a solid mixture after grinding. During heating, the H_{2}WO_{4} firstly transformed into WO_{3} by releasing its coordination water. Afterwards, the salt melted into liquid and accelerated mass transport of the Cs_{x}WO_{3} formation reaction. Meanwhile, the melted salt also isolated precursors and/or products from air, protecting them from oxidization. Figure 3c shows the optical images of sample-A and -B after annealing but before washing. It is obvious that the top surface of sample-A is covered by the molten salt. While the bottom of sample-A is dark blue, indicating the formation of Cs_{x}WO_{3}. The yield of Cs_{x}WO_{3} is determined to be ~ 91.4 % by weight after washing, a high value if being aware of the loss of some product during washing. Different from sample-A, sample-B present a brown color highly alike the raw materials, suggesting the absence of blue-colored...
Figure 4a depicts TEM image of the as-prepared sample-A, which consists of quasi-rectangular microparticles. As functional filters of glass coatings, these micro-scaled particles are so large that serious light scattering will occur, making a clear across-glass vision impossible. By using a bead milling process, the micro-sized particles were comminuted into < 100 nm irregular nano-particles (Figure 4b) with still high crystallinity degree (Figure 4c-d). As further revealed by the particle size distribution curves in dispersion, the pristine Cs$_x$WO$_3$ particles showed a large particle size distribution with an average particle size of 291 nm (d$_{90}$) (Figure 4e). After milling, the particles became small and relatively homogenous in size (average particle size = 152 nm, Figure 4f). The larger average particle sizes in the dispersion than the crystal sizes in TEM image (Figure 4b) could be attributed to particle agglomeration. Figure 4g and 4h show the photographs of the as-prepared sample-A and its aqueous dispersion after bead milling, respectively. It is found that this dispersion is very stable within an observation period of 1 month, highly desired for the further coating process.

In order to determine the optical properties, transmittance spectra of a bare substrate (fused silica glass), and Cs$_x$WO$_3$–PVA coatings of sample-A, -B and C were collected in 300–2500 nm (Figure 5a, 37.7 wt.% Cs$_x$WO$_3$ in the composite films). The bare fused silica glass and the PVA-coating glass were highly transparent (~92%) in all the measured range. For the Cs$_x$WO$_3$–PVA coating of sample-A, however, very different visible (54%) and NIR transparences (6%) were achieved. In other words, this sample can selectively cut off most of the NIR solar energy while keeping a significant visible transparency. When used as window coatings in hot climate, it is expected to depress the solar heat gain and cooling energy consumption of buildings or automobiles. On striking contrary, sample-B is transparent in both visible and NIR range, i.e., without any NIR shielding ability/heat-insulating properties. Figure 5b further exhibits the transmittance profiles of sample-A with different coating thicknesses. By controlling the casting times (from 1 to 4), the integral visible transmittances could be adjusted to be 68, 59, 54 and 45%, corresponding to integral NIR transmittances of 23.3, 8.7, 6.3 and 2.7%, respectively. Inset of Figure 5b shows a typical cross-sectional SEM image of a 3-times casted sample-A coating. The thickness of this coating is 3.766 μm, corresponding to a film thickness of 1.255 μm for each casting time. A typical photograph of a Cs$_x$WO$_3$-coated glass indicate that the coating is very uniform, transparent and clear (Figure 5c-d).

Furthermore, two model houses (40*60*40 cm$^3$, Figure 5e) were constructed to study the thermoregulation effects of Cs$_x$WO$_3$ coatings. In this test, the left and right windows (18*18 cm$^2$) are bare float glass and Cs$_x$WO$_3$-coated glass, respectively. Under simulated solar radiation (R115 lamp, PHILIPS, 245 W), the temperature of the model house with bare glass increased to 40.8 °C after 30 min, which is 7 °C higher than the one with Cs$_x$WO$_3$-coated glass (33.8 °C, Figure 5f). The much lower temperatures of the right room should be attributed to the excellent NIR shielding ability of the Cs$_x$WO$_3$-coated glass. This result suggests that the MSS-prepared Cs$_x$WO$_3$ can be used as functional filters of energy-saving windows in hot climate.

**4. Conclusions**

In conclusion, pure phase Cs$_{0.32}$WO$_3$ were synthesized at 400 °C in air by a molten salt synthesis method. It is found that the molten salt not only promoted the formation of crystalline Cs$_{0.32}$WO$_3$ by accelerating mass transport process, but also prohibited oxidization of obtained Cs$_{0.32}$WO$_3$ by isolating it from air. After casted onto glass substrates, the Cs$_{0.32}$WO$_3$ coatings showed simultaneously a pronounced NIR shielding ability (e.g.,
cut off 94% of NIR light) and a high visible transmittance (e.g., 54%), very suitable for the application as solar control filters. Tested on model houses, a Cs$_{0.32}$WO$_3$ coated glass can depressed the indoor temperature by 7 °C, evidently superior to the bare glass windows.

**Acknowledgements**

The authors thank National Natural Science Foundation of China (51502194), Opening Project of State Key Laboratory of High Performance Ceramics and Superfine Microstructure (SKL201511SIC) and Opening Project of Jiangsu Provincial Engineering Laboratory for Advanced Materials of Salt Chemical Industry (SF201605), and Natural Science Fund for Colleges and Universities in Jiangsu Province (17KJB430004) for financial support.

**Notes and references**


How to cite this article: C. Li, L. Kang, Y. Zhu, Q. Wang, X. Zhao, H. He, D. Tian, and J. Liu, Nano Adv., 2017, 2, 47–52. doi: 10.22180/na216.