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## ARTICLE

## Dependence of infrared absorption property on the Mo doping contents in $M_xWO_3$ with various alkali metals

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Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A series of molybdenum doped tungsten bronzes with various alkali metals were synthesized by solvothermal process using ethanol and acetic acid as solvent. All the diffraction peaks of X-ray diffraction (XRD) for the samples could be indexed as the corresponding kind of hexagonal tungsten bronzes with the formula of  $M_xWO_3$ , based on the M of alkali metal. The targeted research of cesium tungsten bronze indicate that the actual atomic ratio of Cs and W (value of  $x$ ) could be influenced by the introduction of molybdenum, which have a critical effect on the infrared absorption property. The optical tests show that molybdenum doping is an effective process to enhance the absorption of infrared and conversion efficiency of light energy to heat energy for tungsten bronzes with various alkali metals. The optimum starting Mo/W (mol.) to obtain high infrared absorption property were 0.01 for sodium and potassium tungsten bronzes and 0.03 for rubidium and cesium tungsten bronzes, respectively. Among the samples, doped cesium tungsten bronze has the strongest properties.

### Introduction

$M_xWO_3$  is the general formula of nonstoichiometric tungsten bronzes, where the M site is occupied by cations,<sup>1</sup> such as  $H^+$ ,  $NH_4^+$ , alkali and alkaline earth metals. Based on the valence state of tungsten, value of  $x$  is in the range of 0 to 1.  $M_xWO_3$  has tunable crystal structure and chemical composition, which lead to interesting physical and chemical properties, such as superconductivity, electrochromism and humidity sensitivity.<sup>2-4</sup> In recent years, photoresponse properties of  $M_xWO_3$  attract more and more attention.<sup>5-9</sup> It includes transmittance of visible light, absorption of ultraviolet or infrared, conversion of light energy to heat energy, and so on, which has great potential applications in a wide area. Among these properties, infrared absorption is the most significant one.

Mechanism of infrared absorption property for  $M_xWO_3$  is considered to be closely related to the free electrons. In the earlier studies, Skokan<sup>10</sup> pointed out each M cation in  $M_xWO_3$  contributes one electron to the tungsten conduction band. The amount of free electrons could affect the infrared absorption property,<sup>11</sup> which has been confirmed by the research of  $M_xWO_3$  with different content of M cations.<sup>12</sup> In the past few years, most of the reported researches about infrared absorption property of  $M_xWO_3$  focused on different M cations. From the viewpoint of crystal chemistry, these reported tungsten bronzes have almost identical crystalline structures and similar chemical compositions, *i.e.*, a series of isomorphism. Up to

present, there were few works about doping onto the tungsten site and its effects on the infrared absorption property. Doping could cause the crystal structure change to a certain extent, which is possible to raise the content of M cations. Another effect of doping is the potential change of band gap energy, which could contribute to provide more free electrons of  $M_xWO_3$ .

The present paper focuses on the composition, morphology and infrared absorption property of molybdenum doped cesium tungsten bronze synthesized by a facile solvothermal process. Considering that M cations could contribute free electrons to the conduction band and different electronegativities of various alkali metals could result in the different binding energies of electrons, a series of contrast experiments about molybdenum doped  $M_xWO_3$  with other alkali metals (sodium, potassium and rubidium) were also carried out and a brief discussion is provided. On one hand, it can further prove the effect of molybdenum on the optical properties of  $M_xWO_3$ , systematically. On the other hand, investigation of various  $M_xWO_3$  can provide more evidence to demonstrate the relationship between free electrons and infrared absorption property from the perspective of electronegativity, rather than content of alkali metals.

For cesium tungsten bronze, the molybdenum doped sample possesses of higher value of  $x$  with clear rod-like morphology of *ca.* 15 nm in diameter. Comparing to the undoped sample, doped sample has higher near-infrared (NIR) absorbance, lower IR transmittance in a wide wavelength range, and more efficient conversion of light energy to heat energy, while the original high ultraviolet absorbance and visible light transmittance remain basically unchanged. The similar phenomenon can also be observed by other kinds of molybdenum doped tungsten bronzes in our work. By horizontal comparison, doped cesium tungsten bronze has the strongest infrared absorption property among all the samples.

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## Experimental Section

### Synthesis of molybdenum doped tungsten bronzes

Molybdenum doped cesium tungsten bronze were synthesized by a facile solvothermal process. This process reported by Guo *et al.* was used to prepare undoped tungsten bronzes which possess excellent infrared absorption property.<sup>13,14</sup> In our work, 0.15 g of tungsten hexachloride and 0.03 g of cesium hydroxide were dissolved into 20 mL of ethyl alcohol with a certain amount of molybdenum pentachloride. And then, 5 mL of acetic acid was added. The obtained solution was transferred into a Teflon-lined autoclave of 50 mL internal volume, followed by solvothermal reaction in an electric oven at 220 °C for 20 h. After the reaction, the obtained powder was centrifuged, washed 4 times with water and ethanol, respectively, and dried in a drying oven at 60 °C.

Similar solvothermal process were used to prepare sodium, potassium and rubidium tungsten bronzes, using ethyl alcohol, acetic acid, tungsten hexachloride, alkali metal hydroxides and molybdenum pentachloride as the starting materials.

### Characterization

The phase compositions of the samples were determined by X-ray diffraction analysis (XRD, Rigaku D/max 2200 PC) using graphite monochromatized Cu K $\alpha$  radiation. The morphology and microstructure of the particles were investigated using scanning electron microscopy (SEM, JSM-7500F) and transmission electron microscopy (TEM, JEM-2100F). The binding energies of W4f and O1s were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250). Concentrations of elements were determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES, SPECTRO ARCOS EOP).

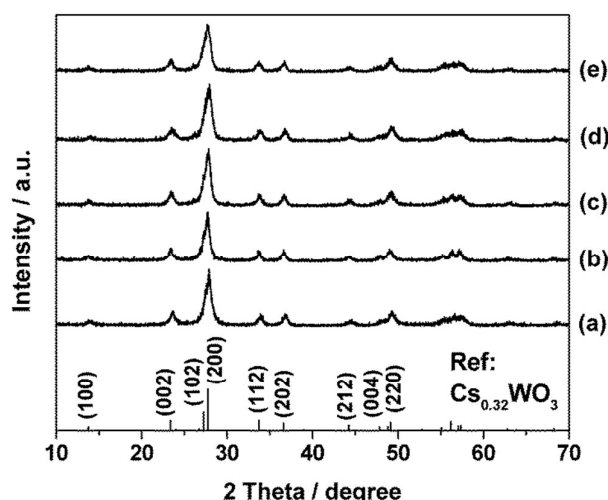
### Optical test

To investigate the infrared absorption property of molybdenum doped tungsten bronzes, optical measurements were employed by an ultraviolet-visible-near infrared spectrophotometer (UV-vis-NIR, UV-3600) and a Fourier transform infrared spectrometer (FT-IR, Tensor 27), respectively. To ensure the results under the same condition, a series of preparatory work were carried out. For the UV-vis-NIR, as-synthesized powder should be stuck to the surface of a sample stage, scraped and blown to form a layer as thin as possible. For the FT-IR, the method is to grind a known mass ratio (100 : 1) of potassium bromide and the sample, and then pressed in a mechanical press with a constant pressure to form a pellet.

To further research the infrared absorption property, samples were irradiated by 50 W halogen lamp for 10 s with quartz glass background, and then the temperature distributions were recorded by a thermal camera (FLIR System i7). To ensure comparability, the distance between lamp and sample, mass and thickness of sample, and room temperature should remain the same.

## Results and discussion

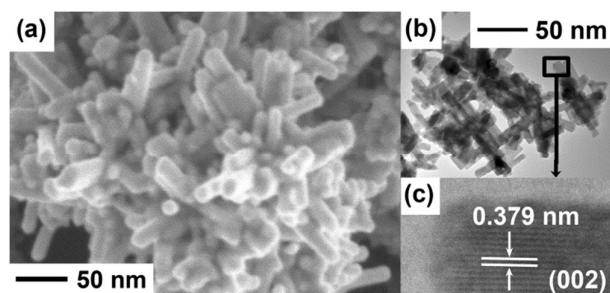
### Characterization of doped cesium tungsten bronze



**Fig. 1.** XRD patterns of cesium tungsten bronzes with Mo/W (mol.) of (a) 0; (b) 0.01; (c) 0.03; (d) 0.05 and (e) 0.1 in the starting materials.

As the focus of this study, cesium tungsten bronze is supposed to possess better infrared absorption property than other tungsten bronzes with various alkali metals because of the lowest electronegativity of cesium. XRD analysis was employed to identify the phase composition and crystallographic structure of cesium tungsten bronze. Fig. 1a – e show the XRD patterns of the samples prepared with the molar ratios of Mo and W from 0 to 0.1 in the starting materials. All the diffraction peaks can be consistent with Cs<sub>0.32</sub>WO<sub>3</sub> (JCPDS card No.83-1334) and there are no peaks of new phases observed. It is worth noting that color of these samples are all blue whether with or without Mo, which might be originated by the chromophore of W<sup>5+</sup>.<sup>15</sup> However, color of the doped samples are deeper than the undoped sample. It suggests that content of W<sup>5+</sup> increased because of the introduction of Mo. In consideration of charge balance, more content of W<sup>5+</sup> means more Cs<sup>+</sup> for cesium tungsten bronze. An in-depth discussion about Mo and reduction of W is to follow.

To obtain more accurate data, further XRD analysis was carried out with a lower scanning speed and adjusted by internal standard method. According to the results of the diffraction peaks, lattice parameter and volume were calculated. Comparing to the undoped sample, for the samples with Mo/W (mol.) of 0.01 and 0.03, it is clear that lattice volume decrease with the introduction of Mo. However, there is no obvious change in grain sizes when the starting Mo/W (mol.) is over 0.03. Consequently, Mo/W (mol.) of 0.03 might be close to a saturation point for doping concentration. To investigate possible impurities in the samples with excessive Mo, a solvothermal reaction was carried out using cesium hydroxide and molybdenum pentachloride only. After this reaction, a small amount of black powder was obtained. The powder might be a kind of cesium-containing molybdenum oxides. There are no obvious XRD peaks could be seen for it, which implies that this powder is an amorphous phase.



**Fig. 2.** (a) SEM, (b) TEM and (c) HR-TEM images of the cesium tungsten bronze prepared with Mo/W (mol.) of 0.03.

The typical morphology of the sample with Mo/W (mol.) of 0.03 was observed by SEM. As exhibited in Fig. 2a, this sample consists of numerous randomly oriented nanorods with diameter from 10 to 20 nm. Further analysis about the morphology and material phase of this sample was carried out by TEM. Fig. 2b and c show the TEM and HR-TEM images. It could be observed that size of rods is consistent with the SEM image (Fig. 2a). According to the HR-TEM image (Fig. 2c), the crystalline interplanar spacing along the direction of the rod was calculated as 0.379 nm, which is identified as the crystallographic plane of (0 0 2) of cesium tungsten bronze.

Although the XRD peaks can be consistent with  $\text{Cs}_{0.32}\text{WO}_3$ , in fact, the molar ratio of Cs and W is lower than 0.32 generally. As mentioned above, this ratio is significant because each  $\text{Cs}^+$  contributes one electron to the tungsten conduction band, which could affect the infrared absorption property. To research the content of cesium, Cs/W (mol.) in the samples without amorphous cesium-containing molybdenum oxides were determined by energy-dispersive X-ray spectrometer (EDS). The results show that Cs/W (mol.) are 0.25, 0.28 and 0.31 nm for the cesium tungsten bronzes with Mo/W (mol.) of 0, 0.01, and 0.03, respectively. The value rises clearly with the introduction of molybdenum and close to the theoretical maximum value of 0.32 when the Mo/W (mol.) reaches saturation of doping concentration.

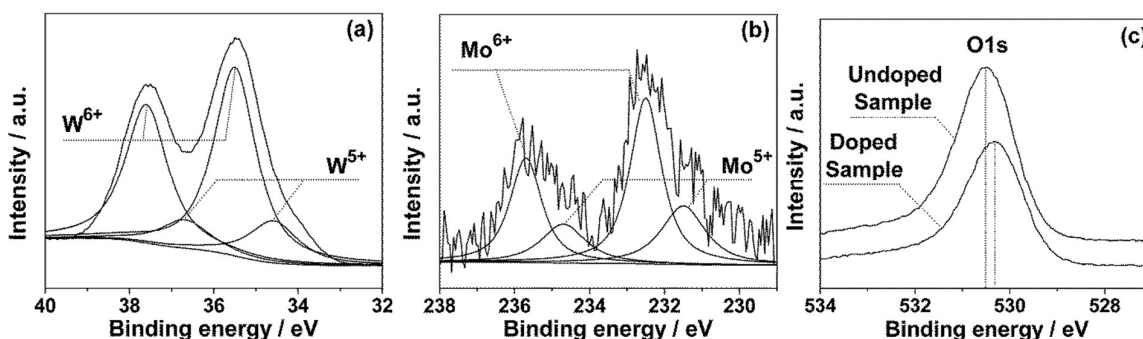
To further investigate the Cs/W (mol.), chemical composition and valence state for cesium tungsten bronze, samples were examined by XPS. Take the sample synthesized with starting Mo/W (mol.) of 0.03 for example, the

result shows that elements of Cs, W and O exist in the sample. For tungsten, a complex energy distribution of W4f photoelectrons was obtained as shown in Fig. 3a. The W4f core-level spectrum could be well fitted into two spin-orbit doublets, corresponding to two different oxidation states of W atoms. This result is consistent with blue color of the sample. Mo3d photoelectrons were also detected by the high resolution scanned spectrum, as shown in Fig. 3b. The fitted result indicates that Mo possess two different oxidation states (6+ and 5+), similar to W. Fig. 3c shows the binding energy of O1s in the samples synthesized with starting Mo/W (mol.) of 0 and 0.03. A shift of the peak towards lower binding energy can be found for specimens with Mo/W (mol.) of 0 and 0.03. It is known that tungsten bronzes structure is built up of cornersharing  $\text{WO}_6$  octahedra,<sup>5</sup> and the electronegativity of Mo is lower than that of W. When Mo doped into cesium tungsten bronze and substituted for a part of W, O formed chemical bonds with Mo, which could give rise to the shielding effect of extranuclear electrons of O decreased, and further caused the binding energy of O1s reduced. On the other hand, the distinction of electronegativity between Mo and W led to electrons polarized and gained more easily by W. It could explain why the doped samples have deeper blue color and the molar ratios of Cs/W increase by doping.

To determine the Mo concentration accurately, sample synthesized with starting Mo/W (mol.) of 0.03 was examined using ICP-AES. In this way, the actual molar ratio of Mo/W (mol.) is 0.05, which is higher than that for the starting materials. It could be explained as the low recovery ratio of W and high recovery ratio of Mo in the solvothermal reaction.

#### Infrared absorption property of doped cesium tungsten bronze

To investigate the infrared absorption property of Mo doped cesium tungsten bronze, an UV-vis-NIR spectrophotometer was employed. Fig. 4 shows the absorbance of the samples prepared with different Mo/W (mol.) from 0 to 0.1 in the wavelength range of 300 – 2100 nm. In the range of 300 – 400 nm, all of samples display a similarly absorbance. For the range of visible light (400 – 780 nm), sample synthesized without Mo has the lowest absorbance comparing with those doped samples, which could be attributable to the depth of color.



**Fig. 3.** XPS spectra of (a) W4f core-level; (b) Mo3d for doped cesium tungsten bronzes synthesized with starting Mo/W (mol.) of 0.03 and (c) XPS spectra of O1s for Mo doped cesium tungsten bronze synthesized with starting Mo/W (mol.) of 0 and 0.03.



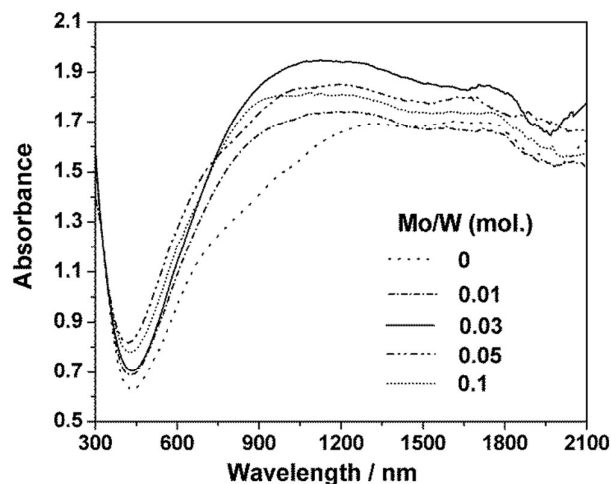


Fig. 4. UV-vis-NIR absorbance of cesium tungsten bronzes with different Mo/W (mol.) in the starting materials.

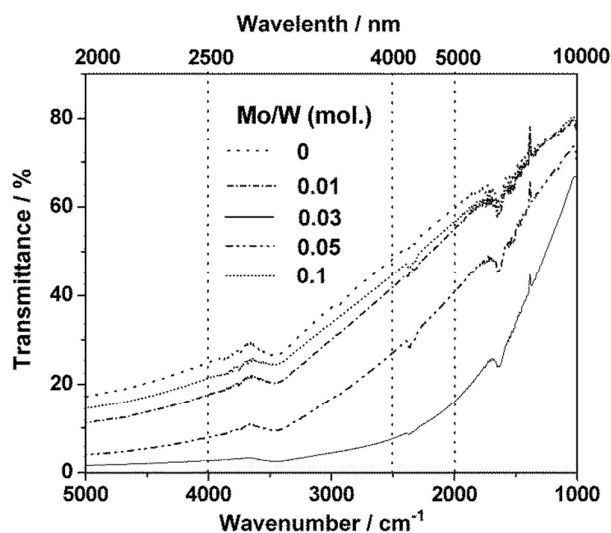


Fig. 5. Infrared transmittances of cesium tungsten bronzes with different Mo/W (mol.) in the starting materials.

Last but most important, in the range of infrared (780 – 2100 nm), absorbance of the undoped sample is still lower than others, while absorbance rises with the introduction of Mo and reaches the highest point when Mo/W (mol.) is 0.03. For the samples prepared with Mo/W (mol.) of 0.05 and 0.1, infrared absorbance declined. It could be related to the amorphous cesium-containing molybdenum oxides formed by the excessive Mo.

As an important parameter of semiconductor, band gap energy could have an effect on the infrared absorption property of the samples according to some known optical absorption mechanisms, such as intrinsic absorption or free carrier absorption. Although it is not obvious in Fig. 4, the absorption edges of the doped cesium tungsten bronzes have a slight red shift comparing to the undoped sample. It implies that the band gap energy could be decreased by doping. Based on the

results of UV-vis-NIR measurement and Tauc plot,<sup>16</sup> the band gap energies were calculated to be 3.03 and 2.95 eV for the undoped cesium tungsten bronze and the sample with Mo/W (mol.) of 0.03, respectively. Decrease of band gap energy caused by doping could contribute to provide more free electrons and further enhance the infrared absorption property to a certain extent. Although the slight change may not be the primary reason for improvement of properties, it is still one of the factors.

To further research the infrared absorption property, another optical analysis was carried out in a wide wavelength range (2000 – 10000 nm) by a FT-IR spectrometer. Fig. 5 shows the infrared transmittance for cesium tungsten bronze synthesized with different Mo/W (mol.) in the starting materials. Lower transmittance implies better infrared absorption property. It clearly reveals that the undoped sample has the highest transmittance and the sample with Mo/W (mol.) of 0.03 is the lowest, which are consistent with the results of UV-vis-NIR measurement.

According to the optical performances in different ranges of wavelength, the sample synthesized with Mo/W (mol.) of 0.03 has a low absorbance of visible light, and more importantly, it has the highest NIR absorbance and lowest IR transmittance compared to other samples with or without Mo. It may be related to the crystal defect and higher content of cesium deriving from saturated molybdenum doping. For the samples prepared with excessive Mo, amorphous cesium-containing molybdenum oxides restrain the infrared absorption properties, potentially.

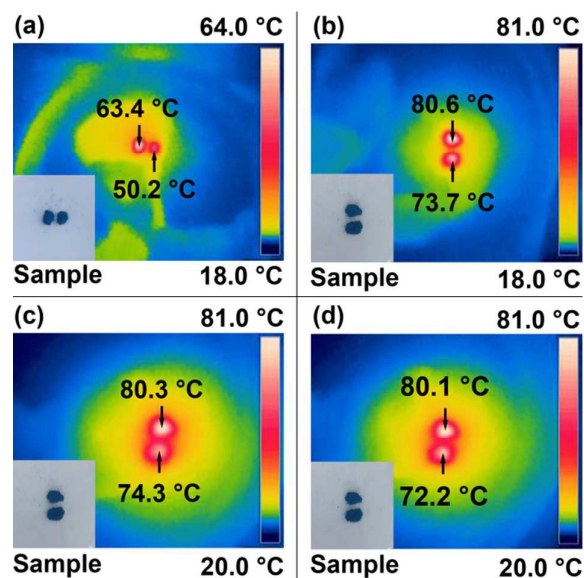


Fig. 6. Thermographic images of the cesium tungsten bronzes (a) without Mo and with Mo/W (mol.) of 0.03 irradiated for (b) 1, (c) 25, and (d) 50 times. Before photographing, the samples were irradiated by 50 W halogen lamp for 10 s starting with the room temperature.

Strong absorption of infrared can give rise to high-efficiency conversion of light energy to heat energy. To display this infrared absorption phenomenon visually, undoped cesium tungsten bronze and the sample prepared with Mo/W (mol.) of 0.03 were irradiated by 50 W halogen lamp for 10 s with quartz glass background, and then the temperature distributions were recorded by a thermal camera. Fig. 6 presents the thermographic images. For the undoped sample (Fig. 6a), irradiation raised the central temperatures of powder piles from room temperature to 63.4 and 50.2 °C, meanwhile, it was not more than 20 °C around the sample, approximately. In comparison, temperatures of the sample prepared with Mo/W (mol.) of 0.03 reached 80.6 and 73.7 °C, whereas the temperature around the sample did not change very much, as shown in Fig. 6b. Furthermore, verification of stability for the doped sample was carried out under the same conditions. The results of repetition for 25 and 50 times are displayed in Fig. 6c and d respectively, which are similar with Fig. 6b. These results indicate that doped sample has a strong and stable infrared absorption property.

#### Doped tungsten bronze with various alkali metals

Similar results of optical measurements could be observed for sodium, potassium and rubidium tungsten bronzes prepared by the same solvothermal process. Comparing to the samples without molybdenum, doped samples have higher NIR absorbance, lower IR transmittance and more efficient conversion of light energy to heat energy, which indicate that molybdenum doping is an effective process to enhance the infrared absorption property. For rubidium tungsten bronze, the optimum starting Mo/W (mol.) to obtain high infrared absorption property is also 0.03, similar to cesium tungsten bronze. However, for sodium and potassium tungsten bronzes, this ratio decreases to 0.01. The distinction of optimum Mo content could be attributed to the ionic radius and steric hindrance. For cesium and rubidium tungsten bronzes, the larger ionic radius of alkali metals lead to W replaced by Mo easily, because ionic radius of Mo is smaller than W.

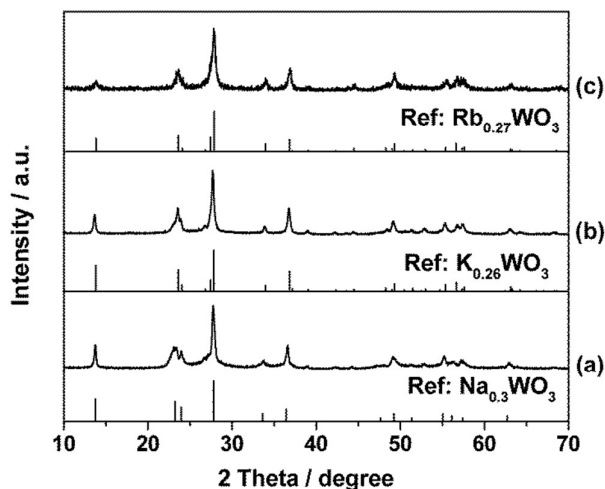


Fig. 7. XRD patterns of (a) sodium, (b) potassium and (c) rubidium tungsten bronzes with the optimum Mo/W (mol.).

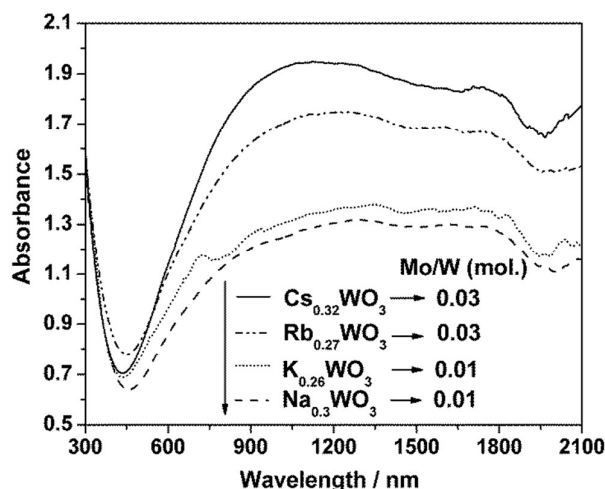


Fig. 8. UV-vis-NIR absorbance of various tungsten bronzes with the optimum Mo/W (mol.).

Fig. 7a – c exhibit the XRD patterns of sodium, potassium and rubidium tungsten bronzes with the optimum Mo/W (mol.). These diffraction peaks can be consistent with  $\text{Na}_{0.3}\text{WO}_3$  (JCPDS card No.46-0174),  $\text{K}_{0.26}\text{WO}_3$  (JCPDS card No.83-1593), and  $\text{Rb}_{0.27}\text{WO}_3$  (JCPDS card No.73-1549), respectively, without other phases.

To further research the infrared absorption property of various doped tungsten bronzes, horizontal comparisons of samples with the optimum Mo/W (mol.) are carried out, as shown in Fig. 8. The order of IR absorbance from high to low is cesium, rubidium, potassium and sodium tungsten bronzes. On the one hand, this order could be related to the doping concentration. For cesium and rubidium tungsten bronzes, higher Mo/W (mol.) may lead to more crystallographic defects and further decrease of band gap energy to a certain extent. On the other hand, this order is consistent with the intensity of electronegativity of alkali metals which directly affects the free electrons in tungsten bronze. As discussed in the introduction, infrared absorption property is closely related to the free electrons. Although free electrons could also be affected by doping and value of  $x$ , electronegativity of alkali metals might be the main factor for free electrons of various tungsten bronzes in our work, considering the slight change of band gap energy caused by doping and higher IR absorbance of doped  $\text{K}_{0.26}\text{WO}_3$  compared to  $\text{Na}_{0.3}\text{WO}_3$ .

There were some noteworthy phenomena for sodium and potassium tungsten bronzes. Unlike cesium and rubidium tungsten bronzes, color of undoped sodium and potassium tungsten bronzes were much lighter than other samples with or without molybdenum, their infrared absorption properties were also particularly weak, and would lose the blue color gradually in the air after several days. According to these phenomena, for the undoped sodium and potassium tungsten bronzes synthesized by this solvothermal process, the actual content of  $\text{Na}^+$  or  $\text{K}^+$  might be very low, *i.e.*, relatively few  $\text{W}^{6+}$  were reduced although their XRD peaks can be consistent with  $\text{Na}_{0.3}\text{WO}_3$  and  $\text{K}_{0.26}\text{WO}_3$  respectively. Moreover, they could be easily oxidized. However, molybdenum doped sodium and potassium tungsten bronzes possess deep and steady blue color. As

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a result, their infrared absorption properties are much stronger than those two undoped samples, although they are still weaker than cesium and rubidium tungsten bronzes as shown in Fig. 8. It suggests that Mo is indeed effective in stability of  $W^{5+}$  in tungsten bronzes. Probably, it is related to both the electronegativity and size of molybdenum and tungsten.

### Conclusions

Mo doped cesium tungsten bronze was successfully synthesized by the solvothermal process. On the one hand, introduction of molybdenum led to the increase of value of  $x$  and decrease of band energy, which provided the possibility of enhancement for the infrared absorption property. On the other hand, however, excessive concentration of Mo formed amorphous cesium-containing molybdenum oxides and restrained the infrared absorption property. When the actual Mo/W (mol.) reached 0.05, *i.e.*, the starting Mo/W (mol.) of 0.03, morphology of the sample was uniform rod-like particles in diameter of *ca.* 15 nm. Comparing to all the cesium tungsten bronzes with or without molybdenum, this sample exhibited highest NIR absorbance, lowest IR transmittance in a wide wavelength range and more efficient conversion of light energy to heat energy, while the original high ultraviolet absorbance and visible light transmittance remain basically unchanged.

The similar phenomenon can also be observed by other kinds of molybdenum doped tungsten bronzes with various alkali metals in our work, which indicated that molybdenum doping is an effective process to enhance the infrared absorption property. The optimum starting Mo/W (mol.) were 0.01 for sodium and potassium tungsten bronzes and 0.03 for rubidium tungsten bronze, respectively. By horizontal comparison, doped cesium tungsten bronze has the strongest infrared absorption property among all the samples, which caused by a combined effect of doping concentration, value of  $x$  in  $M_xWO_3$  and electronegativity of alkali metals.

### Acknowledgements

The authors appreciate the financial support from the National Science Foundation of China (NSFC51372006); the Scientific Research Starting Foundation for Returned Overseas Chinese Scholars, Ministry of Education; the Start-Up Fund for High-End Returned Overseas Talents (Renshetinghan 2010, No. 411), Ministry of Human Resources and Social Security, China and the Lab-Installation Foundation of Beihang University for New Teachers.

### Notes and references

- 1 I. M. Szilágyi, J. Madarász, G. Pokol, F. Hange, G. Szalontai, Katalin Varga-Josepovits and A. L. Tóth, *J. Therm. Anal. Calorim.*, 2009, **97**, 11.
- 2 C. J. Raub, A. R. Sweedler, M. A. Jensen, S. Broadston, and B. T. Matthias, *Phys. Rev. Lett.*, 1964, **13**, 746.
- 3 K. Adachi, Y. Ota, H. Tanaka, M. Okada, N. Oshimura and A. Tofuku, *J. Appl. Phys.*, 2013, **114**, 194304.
- 4 I. Tsuyumoto and T. Kudo, *Sens. Actuators B*, 1996, **30**, 95.
- 5 C. S. Guo, S. Yin, L. Huang and T. Sato, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2794.
- 6 C. S. Guo, S. Yin, Q. Dong and T. Sato, *Nanoscale*, 2012, **4**, 3394.

- 7 T. M. Mattox, A. Bergerud, A. Agrawal and D. J. Milliron, *Chem. Mater.*, 2014, **26**, 1779.
- 8 Y. Sato, M. Terauchi and K. Adachi, *J. Appl. Phys.*, 2012, **112**, 074308.
- 9 K. Adachi, *J. Mater. Res.*, 2012, **27**, 965.
- 10 M. R. Skokan, W. G. Moulton and R. C. Morris, *Phys. Rev. B*, 1979, **20**, 3670.
- 11 H. Takeda and K. Adachi, *J. Am. Ceram. Soc.*, 2007, **90**, 4059.
- 12 C. S. Guo, S. Yin, M. Yan and T. Sato, *J. Mater. Chem.*, 2011, **21**, 5099.
- 13 C. S. Guo, S. Yin, P. Zhang, M. Yan, K. Adachi, T. Chonan and T. Sato, *J. Mater. Chem.*, 2010, **20**, 8227.
- 14 C. S. Guo, S. Yin, K. Adachi, T. Chonan and T. Sato, *IOP Conf. Series: Mater. Sci. Eng.* 2011, **18**, 032014.
- 15 K. Bange, *Sol. Energy Mater. Sol. Cells*, 1999, **58**, 1.
- 16 J. Tauc, R. Grigorovici and A. Vancu, *Phys. Status Solidi B*, 1966, **15**, 627.

## Graphical abstract

Mo doping is an effective process to enhance the infrared absorption property for  $M_xWO_3$  with various alkali metals.

