Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 2675–2678

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis of $NiWO_4$ nano-particles in low-temperature molten salt medium

Zuwei Song [a,b,c], Junfeng Ma [b,*], Huyuan Sun [a,**], Wei Wang [a,c],
Yong Sun [b], Lijuan Sun [a], Zhengsen Liu [b], Chang Gao [b]

[a] *Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266003, PR China*
[b] *State Key Lab. of Green Building Materials, China Building Materials Academy, Beijing 100024, PR China*
[c] *Graduate University, Chinese Academy of Sciences, Beijing 100049, PR China*

Received 28 August 2008; received in revised form 12 January 2009; accepted 1 March 2009
Available online 27 March 2009

Abstract

Nickel tungstate ($NiWO_4$) nano-particles were successfully synthesized at low temperatures by a molten salt method, and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and ultraviolet visible spectra techniques (UV–vis), respectively. The effects of calcining temperature and salt quantity on the crystallization and development of $NiWO_4$ crystallites were studied. Experimental results showed that the well-crystallized $NiWO_4$ nano-particles with about 30 nm in diameter could be prepared at 270 °C with 6:1 mass ratio of the salt to $NiWO_4$ precursor. XRD analysis confirmed that the product was a pure monoclinic phase of $NiWO_4$ with wolframite structure. UV–vis spectrum revealed that $NiWO_4$ nano-particles had good light absorption properties in both ultraviolet and visible light region.

Keywords: $NiWO_4$; Nano-particle; Low temperature; Molten salt method

1. Introduction

Nickel tungstate ($NiWO_4$), as one of the important inorganic materials in metal tungstate families, is commonly used for catalysts [1–3] and humidity sensors [4] due to its attractive catalytic activity and good sensitivity to humidity. Moreover, $NiWO_4$ has been studied extensively in other potential applications such as microwave devices [5] and photoanodes [6,7]. To obtain $NiWO_4$ materials with high performance, the key step is how to synthesize $NiWO_4$ powders with high chemical purity and good phase composition. Recently, $NiWO_4$ nano-particles have attracted much attention because of their large surface area and remarkable quantum size effect, which result in lower sinter temperature and better photocatalytic activity [8–10].

Various techniques have been developed to synthesize $NiWO_4$ particles. In general, they are prepared at high temperatures above 900 °C by solid-state reaction method [11,12], in which the repeated calcining–crushing cycles are needed to complete chemical reactions. It would consume a large amount of energy. In addition, $NiWO_4$ particles prepared by the solid-state reaction method are always relatively large particle size, irregular morphology and impure chemical composition, which would bring about a negative effect on their application. Recently developed wet chemical methods seemed to overcome these disadvantages, where reacting constituents could be well mixed on the atomic level in aqueous solutions, e.g. co-precipitation [13,14], modified citrate complex technique [15,16] and hydrothermal method [17], which have been employed for the preparation of fine $NiWO_4$ particles. However, the precipitate and the citrate complex precursors obtained in advance still need further calcination at relatively high temperatures. Though hydrothermal synthesis is well known as a soft solution process and presents so many advantages as low synthetic temperature and good crystallinity of products [18], the requirement of specific autoclave and the low output limit its wide-application. Therefore, it is necessary

---

* Corresponding author. Tel.: +86 10 51167477; fax: +86 10 65761714.
** Corresponding author. Tel.: +86 532 82898732; fax: +86 532 82898732.
E-mail addresses: majunfengcbma@yahoo.com.cn (J. Ma), sun@ms.qdio.ac.cn (H. Sun).

0272-8842/$36.00 © 2009 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2009.03.010

to explore new routes to synthesize $NiWO_4$ nano-particles, especially for the mass-production.

In this paper, the synthesis of $NiWO_4$ nano-particles with perfectly crystalline morphology by a molten salt method at low temperatures was reported, and the processing parameters initially optimized. Compared with other routes, this method has such advantages as simple instrumentation, low reaction temperature and easy manipulation. It will be beneficial to realizing the large-scale production of $NiWO_4$ nano-particles. To the author's knowledge, no such studies have ever been reported.

2. Experimental

Analytical $Na_2WO_4{\cdot}2H_2O$ and $Ni(NO_3)_2{\cdot}6H_2O$ were used as starting materials. Appropriate amounts of them were dissolved in distilled water to form aqueous solutions with 1 M concentration, respectively. Under strongly magnetic stirring at room temperature, the two solutions were mixed together and a precipitate was formed. The precipitate was filtered and washed with distilled water for several times, and dried in an oven at 60 °C for 5 h to obtain a $NiWO_4$ precursor. By ball milling in ethanol for 0.5 h, the $NiWO_4$ precursor was mixed with a salt-mixture composed of 46 wt.% $NaNO_3$ and 54 wt.% $LiNO_3$, where the mass ratio of the salt to the $NiWO_4$ precursor were 0:1, 3:1, 6:1 and 12:1, respectively. The mixtures were put into Al_2O_3 crucibles and then heated at different temperatures for the same holding time of 8 h. Finally, the resultant products were dissolved into hot distilled water of ca. 40 °C and filtered with vacuum filtration, followed by washing with distilled water for three times, and once with ethanol, then dried at 60 °C for 3 h in the air.

The phase composition was determined using an X-ray powder diffractometer (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation. The particle size and morphology of the as-prepared samples were observed using a transmission electron microscope (TEM, JEM-1200EX, JEOL Ltd., Japan). The ultraviolet visible spectra were recorded on a UV–vis spectrophotometer (UV-3101PC, Japan).

3. Results and discussion

Fig. 1 shows XRD patterns of samples prepared by the molten salt method at 210, 270, and 340 °C for 8 h, respectively. The mass ratio of the salt to the $NiWO_4$ precursor is 6:1. Obviously, all XRD patterns can be indexed to monoclinic $NiWO_4$ with wolframite structure, well matched with the reported data (JCPDS: 15-0755).

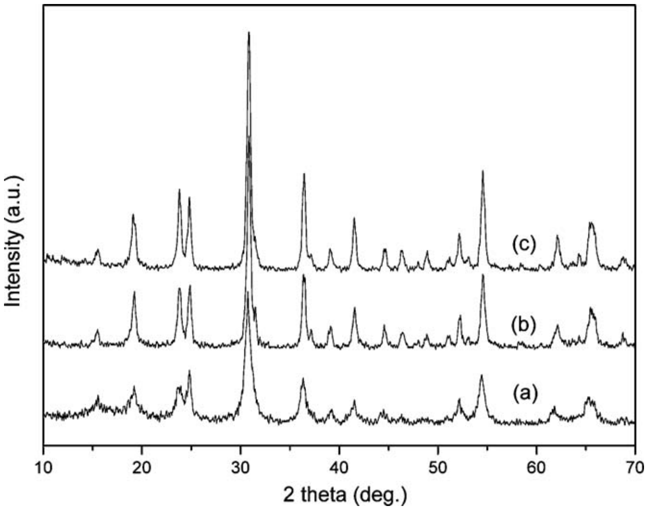

Fig. 1. XRD patterns of samples prepared by the molten salt method at (a) 210 °C; (b) 270 °C; and (c) 340 °C for 8 h, respectively.

As shown in Fig. 1(a), the crystallized product obtained at 210 °C has extremely fine particle size, which can be confirmed by its broad X-ray diffraction peaks. With an increase of calcining temperature to 270 °C, the XRD pattern in Fig. 1(b) displays the obvious improvement of $NiWO_4$ phase in crystallinity. It shows that good crystallinity and large sizes of $NiWO_4$ crystallites could be obtained at this temperature. When the calcining temperature was increased to 340 °C, the diffraction peaks become stronger and sharper, which implies that increasing the calcining temperature would promote the crystallization and growth of $NiWO_4$ crystallites. The reason can be explained as follows. At 210 °C, the salt-mixture with the melting point of 193 °C [19] can offer a low viscosity liquid environment, which is favorable to mass and heat transfer in the reaction process, thus greatly decreases the synthetic temperature of $NiWO_4$ nano-particles compared with the solid-state reaction method. Moreover, the further elevation of the calcining temperature would strengthen the tendency accelerating the mutual reaction between constituents and improving their crystallinity. Therefore, the formation of $NiWO_4$ crystallites with higher crystallinity and larger particle size can be expected at 340 °C.

In addition, the position of X-ray diffraction peaks at 210 °C shifts a little to the left, compared with the other two X-ray diffraction patterns at higher temperatures (270 and 340 °C). It is possibly related to the lower crystallinity of $NiWO_4$ sample prepared at 210 °C. The similar phenomenon is also found in Ref. [13].

Fig. 2 presents TEM micrographs of $NiWO_4$ powders obtained by the molten salt method at 210, 270, and 340 °C for 8 h, respectively. It is clear that the as-prepared $NiWO_4$ samples are composed of nano-sized particles. $NiWO_4$ nano-particles synthesized at 210 °C (Fig. 2(a)) show a little soft-aggregated with the smallest average particle size about 5 nm, while ones obtained respectively at 270 °C (Fig. 2(b)) and 340 °C (Fig. 2(c)) are of larger particle sizes and better crystallinity, and both of them consist of homogeneous and nearly spherical grains. The former is ca. 30 nm in diameter, the latter increases to ca. 50 nm in average particle size. TEM observation results are well consistent with the above XRD analysis, i.e. high calcining temperature would promote the crystallization and growth of $NiWO_4$ nano-particles in the range of 210–340 °C. Nevertheless, except for large energy consumption, excessively elevating the calcining temperature would lead to the undue growth and hard aggregation of $NiWO_4$ nano-particles, which would bring about negative effects on their performance [10]. Therefore, our studies suggested that 270 °C is adequate to the formation of high quality $NiWO_4$ nano-particles with good crystallinity and perfect morphology under the molten salt condition.

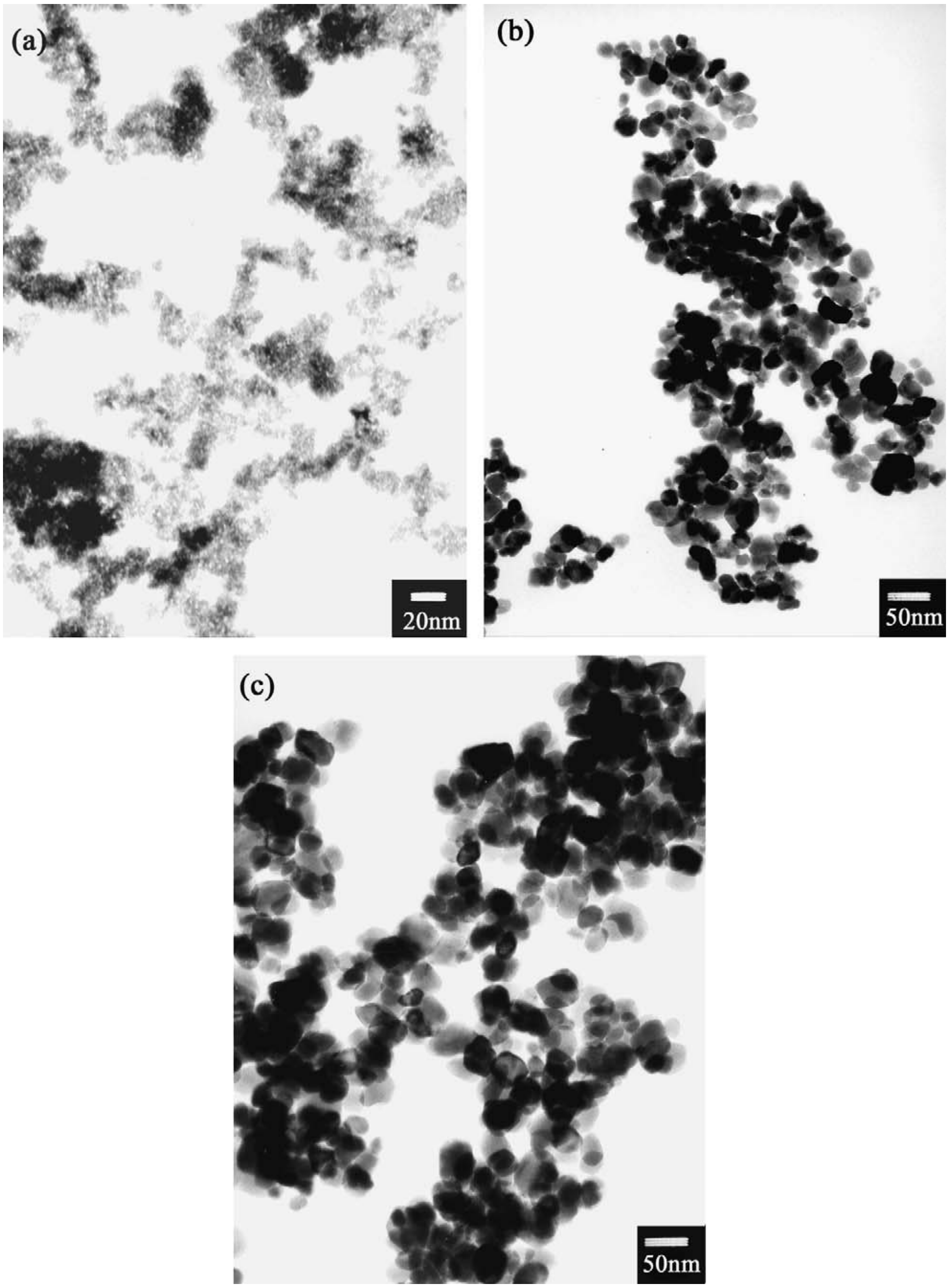

Fig. 2. TEM images of $NiWO_4$ samples obtained by the molten salt method at (a) 210 °C; (b) 270 °C; and (c) 340 °C for 8 h, respectively (with 6:1 mass ratio of the salt to the $NiWO_4$ precursor).

Fig. 3 shows XRD patterns of samples synthesized by the molten salt method at 270 °C for 8 h with various mass ratios of the salt to the $NiWO_4$ precursor: 0:1, 3:1, 6:1 and 12:1. $NiWO_4$ phase could not be obtained without using the molten salt, only can an amorphous phase be found, as shown in Fig. 3(a). It reveals that the molten salt medium plays an important role in the low-temperature synthesis of $NiWO_4$ nano-particles. The other three XRD patterns, which can be confirmed to be monoclinic $NiWO_4$, are similar except for the intensity of the diffraction peaks, as shown in Fig. 3(b)–(d). A remarkable increase in XRD intensity can be observed from 3:1 to 6:1, whereas further increasing the ratio of the salt to the precursor to 12:1 does not give rise to obvious change in intensity. Therefore, it seems that the mass ratio of 6:1 would meet the needs for the crystallization and development of $NiWO_4$ crystallites. It is for this reason that 6:1 was chosen as the optimized mass ratio of the salt to the $NiWO_4$ precursor.

Fig. 4 shows a typical UV–vis absorption spectrum of $NiWO_4$ nano-particles, which were synthesized by the molten salt method at 270 °C with a holding time of 8 h under the condition of 6:1 mass ratio. The onset of the absorption locates at about 420 nm, showing a red-shift of ca. 60 nm relative to the reported data [6]. The similar red-shift results, arisen from the difference in particle size, also appeared in the preparation of $Bi_4Ti_3O_{12}$ nano-particles [20]. It reveals that $NiWO_4$ nano-

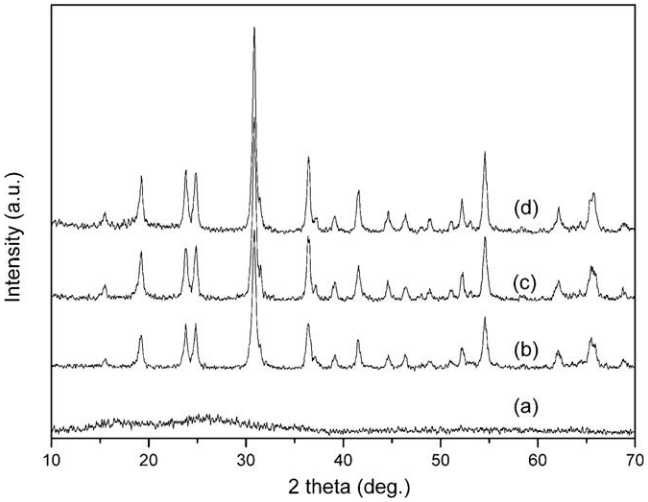

Fig. 3. XRD patterns of samples prepared by the molten salt method at 270 °C for 8 h with the different mass ratios of the salt to the $NiWO_4$ precursor: (a) 0:1, (b) 3:1, (c) 6:1, and (d) 12:1.

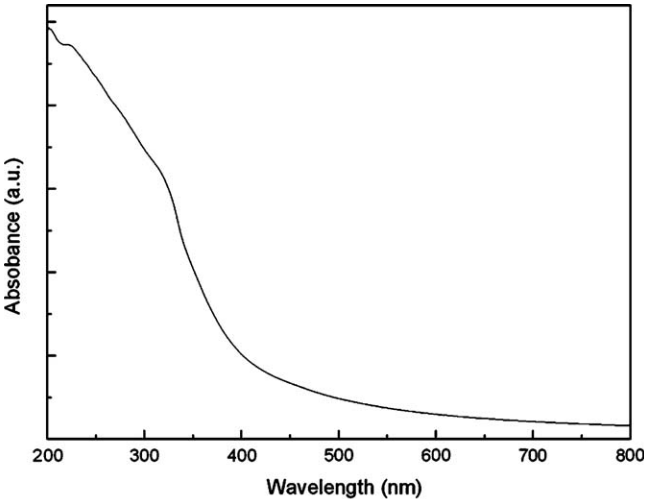

Fig. 4. UV–vis absorption spectrum of $NiWO_4$ nano-particles obtained by the molten salt method at 270 °C for 8 h (the mass ratio of the salt to the $NiWO_4$ precursor: 6:1).

particles have good light absorption properties not only in the ultraviolet but also in the visible light region.

4. Conclusions

The synthetic temperature of $NiWO_4$ crystallites can be greatly lowered by introducing a molten salt medium in reaction process. Well-crystallized $NiWO_4$ nano-particles with ca. 30 nm in diameter could be successfully prepared by our molten salt method at a temperature as low as 270 °C, where the mixture of $NaNO_3$ and $LiNO_3$ was used as the molten salt medium with 6:1 mass ratio of the salt to the $NiWO_4$ precursor. The as-prepared $NiWO_4$ nano-particles exhibit good light absorption properties in both ultraviolet and visible light region.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant No.50772105).

References

[1] B. Scheffer, P. Molhoek, J.A. Moulijn, Temperature-programmed reduction of NiO–WO_3/Al_2O_3 hydrodesulphurization catalysts, Appl. Catal. 46 (1) (1989) 11–30.

[2] R.A. Diaz-Real, R.S. Mann, I.S. Sambi, Hydrotreatment of Athabasca bitumen derived gas oil over nickel–molybdenum, nickel–tungsten, and cobalt–molybdenum catalysts, Ind. Eng. Chem. Res. 32 (1993) 1354–1358.

[3] D.L. Stern, R.K. Grasselli, Propane oxydehydrogenation over metal tungstates, J. Catal. 167 (1997) 570–572.

[4] A.K. Bhattacharya, R.G. Biswas, A. Hartridge, Environment sensitive impedance spectroscopy and dc conductivity measurements on $NiWO_4$, J. Mater. Sci. 32 (1997) 353–356.

[5] R.C. Pullar, S. Farrah, N.McN. Alford, $MgWO_4$, $ZnWO_4$, $NiWO_4$ and $CoWO_4$ microwave dielectric ceramics, J. Eur. Ceram. Soc. 27 (2007) 1059–1063.

[6] T. Ejima, T. Banse, H. Takatsuka, Y. Kondo, M. Ishino, N. Kimura, M. Watanabe, I. Matsubara, Microscopic optical and photoelectron measurements of MWO_4 (M = Mn, Fe, and Ni), J. Lumin. 119–120 (2006) 59–63.

[7] P.S. Pandey, N.S. Bhave, R.B. Kharat, Structural, optical, electrical and photovoltaic electrochemical characterization of $NiWO_4$ thin films, Electrochim. Acta 51 (2006) 4659–4664.

[8] M.N. Mancheva, R.S. Iordanova, D.G. Klissurski, G.T. Tyuliev, B.N. Kunev, Direct mechanochemical synthesis of nanocrystalline $NiWO_4$, J. Phys. Chem. C 111 (2007) 1101–1104.

[9] A. Kuzmin, J. Purans, Local atomic and electronic structure of tungsten ions in AWO_4 crystals of scheelite and wolframite types, Rad. Meas. 33 (2001) 583–586.

[10] A. Kuzmin, J. Purans, R. Kalendarev, D. Pailharey, Y. Mathey, XAS, XRD, AFM and Raman studies of nickel tungstate electrochromic thin films, Electrochim. Acta 46 (2001) 2233–2236.

[11] Q.T. Guo, J.W. Wang, O.J. Kleppa, Note on the enthalpies of formation, from the component oxides, of $CoWO_4$ and $NiWO_4$, determined by high-temperature direct synthesis calorimetry, Thermochim. Acta 380 (2001) 1–4.

[12] K.T. Jacob, Phase relationships in the system Ni–W–O and thermodynamic properties of $NiWO_4$, J. Mater. Sci. 12 (1977) 1647–1652.

[13] J.M. Quintana-Melgoza, J. Cruz-Reyes, M. Avalos-Borja, Synthesis and characterization of $NiWO_4$ crystals, Mater. Lett. 47 (2001) 314–318.

[14] A. Sen, P. Pramanik, A chemical synthetic route for the preparation of fine-grained metal tungstate powders (M = Ca, Co, Ni, Cu, Zn), J. Eur. Ceram. Soc. 21 (2001) 745–750.

[15] J.H. Ryu, J.-W. Yoon, C.S. Lim, W.C. Oh, K.B. Shim, Microwave-assisted synthesis of nanocrystalline MWO_4 (M:Ca, Ni) via water-based citrate complex precursor, Ceram. Int. 31 (2005) 883–886.

[16] J.H. Ryu, J.-W. Yoon, C.S. Lim, K.B. Shim, Microwave-assisted synthesis of MWO_4 and $MMoO_4$ (M = Ca, Ni) nano-powders using citrate complex precursor, Key Eng. Mater. 317–318 (2006) 223–226.

[17] A. Dias, V.S.T. Ciminelli, Thermodynamic calculations and modeling of the hydrothermal synthesis of nickel tungstates, J. Eur. Ceram. Soc. 21 (2001) 2061–2065.

[18] S. Somiya, R. Roy, Hydrothermal synthesis of fine oxide powders, Bull. Mater. Sci. 23 (2000) 453–460.

[19] R. Xu, Synthesis and Preparation in Inorganic Chemistry, Higher Education Press, Beijing, 2001, pp. 199.

[20] L.J. Xie, J.F. Ma, Z.Q. Zhao, H. Tian, J. Zhou, Y.G. Wang, J.T. Tao, X.Y. Zhu, A novel method for the preparation of $Bi_4Ti_3O_{12}$ nanoparticles in w/o microemulsion, Colloids Surf. A: Physicochem Eng. Aspects 280 (2006) 232–236.