Physica B 411 (2013) 173–177

Contents lists available at SciVerse ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Study of the structures and thermal expansion properties of solid solutions $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$ and $1.8\le x\le 2.0$)

Ying Zhi Cheng [a,b], Xiao Ling Xiao [b,*], Xiang Feng Liu [b], Mei Mei Wu [c], Jie Peng [d], Zhong Bo Hu [b,*]

[a] College of Chemical Engineering, Shandong University of Technology, Zibo 255049, China
[b] College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing 100049, China
[c] China Institute of Atomic Energy, Beijing 102413, China
[d] Institute of High Energy Physics, Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:
Received 23 July 2012
Received in revised form
4 December 2012
Accepted 5 December 2012
Available online 12 December 2012

Keywords:
Thermal expansion
Crystal structure
X-ray diffraction
Rietveld method

ABSTRACT

Here a new series of solid solutions $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$ and $1.8\le x\le 2.0$) are prepared by conventional solid-state reaction. Their crystal structures and thermal expansion properties are studied using X-ray diffraction and thermal analysis. It is found that $Yb_{2-x}Dy_xW_3O_{12}$ with $0\le x\le 1.5$ adopt orthorhombic structure and show a negative thermal expansion (NTE) in temperature range of 200–800 °C, with lattice parameters *a*, *b* and *c* all contracting as temperature increases. The substitution of dysprosium for ytterbium results in stronger NTE in $Yb_{2-x}Dy_xW_3O_{12}$ comparing to that in $Yb_2W_3O_{12}$. On the other hand, compounds of $Yb_{2-x}Dy_xW_3O_{12}$ with $1.8\le x\le 2.0$ adopt monoclinic structure and show positive thermal expansion in the 25–800 °C range. The different crystal structures lead to the observed different thermal expansion behaviors in $Yb_{2-x}Dy_xW_3O_{12}$. Thus, the thermal expansion properties of $Yb_{2-x}Dy_xW_3O_{12}$ can be controlled by careful adjusting of *x*.

1. Introduction

Recently, more attentions are focused on negative thermal expansion (NTE) materials due to their wide applications from the high-tech to the mundane including electronic components, printed circuit boards, optical substrates, cookware and so on [1–6]. In addition to the well-known NZP and ZrW_2O_8 families, $A_2(WO_4)_3$ (A site is rare earth cation) [7–12] is another important family of NTE materials with advantages including that the A site is considerably flexible to accommodate various trivalent ions ranging from Al to Gd [7,13]. If site A is partly substituted by some other trivalent ions B^{3+}, the resulting solutions $A_{2-x}B_x(WO_4)_3$ may show quite different thermal properties, which, in theory, offers a possible way to adjust the thermal expansion coefficients of $A_{2-x}B_x(WO_4)_3$ to any desired value including zero [9].

Indeed, our previous works have also proved that the thermal expansion properties of solid solution $A_{2-x}B_x(WO_4)_3$ can be adjusted through site A partly substituted by some other trivalent ions B^{3+}. For example, Er in $Er_2W_3O_{12}$ is substituted by larger cations in forming solid solutions $Er_{2-x}B_xW_3O_{12}$ (B=Sm [14], Nd [15], Ce [16] and Dy [17]), where the crystal structure and thermal expansion properties of this kind of materials can be adjusted. Generally, compounds $Er_{2-x}B_xW_3O_{12}$ show negative or positive thermal expansion properties according to their crystal structure adopting orthorhombic or monoclinic structure. The thermal expansion properties of these compounds are intimately relevant with the structure features like sharing of polyhedral edges or corners. As reported by Sumithra et al. [18], $Yb_2W_3O_{12}$ adopts similar orthorhombic structure to $Y_2W_3O_{12}$ and its thermal expansion coefficient α_l is $-6.38\times 10^{-6}\,{}^{\circ}C^{-1}$ for temperature from 200 to 800 °C. The next year, Sumithra and Umarji [11] reported that $Dy_2W_3O_{12}$ exhibits positive thermal expansion with monoclinic structure and shows a α_l of $7.63\times 10^{-6}\,{}^{\circ}C^{-1}$ from room temperature (RT) to 800 °C. Thus it is interesting to study the structures and thermal properties of compounds $Yb_{2-x}Dy_xW_3O_{12}$ and in this paper we present our work on synthesis, structures and thermal expansion properties of $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$ and $1.8\le x\le 2.0$). And we hope the thermal expansion properties of $Yb_{2-x}Dy_xW_3O_{12}$ can be adjusted by careful changing of *x*.

2. Material and methods

Samples $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 2.0$) were prepared by conventional solid-state reaction from a mixture of Yb_2O_3 (purity 99.95%), Dy_2O_3 (purity 99.9%) and WO_3 (purity 99.5%). All the

---

[*] Corresponding authors. Tel./fax: +86 10 8825 6328.
E-mail addresses: chengyz@sdut.edu.cn (Y.Z. Cheng), xlxiao@ucas.ac.cn, sdourmail@163.com (X.L. Xiao), liuxf@ucas.ac.cn (X.F. Liu), wmm04b@mails.ucas.ac.cn (M.M. Wu), pengjie@mails.ucas.ac.cn (J. Peng), huzq@ucas.ac.cn (Z.B. Hu).

0921-4526/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.physb.2012.12.006

starting materials were preheated to 500 °C before weighting to protect from H_2O and CO_2. Stoichiometric ratio of the reactants were thoroughly grounded and calcined at 900 °C for 24 h, then 1000 °C for 24 h with intermediate regrinding. The room temperature X-ray diffraction data were recorded on MSAL-XD2 using Cu K_α radiation at Laboratory of Inorganic Materials of Graduate University of the Chinese Academy of Sciences. The high temperature XRD data were collected on PANalytical X'Pert PRO MPD with Cu K_α radiation at Beijing Normal University. The heating speed was 30 °C min^{-1} and data were collected after the temperature was kept for 5 min.

The thermogravimetric (TG) and differential thermal analysis (DTA) of $Yb_{2-x}Dy_xW_3O_{12}$ ($x=1.8$ and 2.0) were performed in air from RT to 1100 °C at National Laboratory of Rare Earth Material Chemistry and Application of Peking University. The heating rate was 10 °C min^{-1}. The sintered aluminum oxide powder was used as a reference material.

3. Results and discussion

3.1. Phase formation by room temperature X-ray diffraction

The room temperature X-ray powder diffraction patterns of $Yb_{2-x}Dy_xW_3O_{12}$ indicate that for $0\le x\le 1.5$, solid solutions $Yb_{2-x}Dy_xW_3O_{12}$ adopt the $Yb_2W_3O_{12}$ structure, in which the Yb cations have a coordination number of 6 and the compounds crystallize in corner-shared orthorhombic space group Pnca. For $1.8\le x\le 2.0$, solid solutions $Yb_{2-x}Dy_xW_3O_{12}$ adopt the $Dy_2W_3O_{12}$ structure, in which the Dy cations have a coordination number of 8 and the compounds crystallize in edge-shared monoclinic space group C2/c. For $1.5<x<1.8$, no single phase sample can be successfully prepared. There is somewhere in between $x=1.5$ and $x=1.8$ a first-order transition from the $Yb_2W_3O_{12}$ structure to that of $Dy_2W_3O_{12}$.

All diffraction patterns were refined using the FULLPROF software (Rietveld method) [17], without any constrains on atomic coordinates parameters. Compounds $Yb_{2-x}Dy_xW_3O_{12}$ with $0\le x\le 1.5$ and $1.8\le x\le 2.0$ were refined using the atomic coordinates of $Y_2W_3O_{12}$ [5] and $Dy_2W_3O_{12}$ [19] as the starting structure models, respectively. As examples, the refined results of $Yb_{1.2}Dy_{0.8}W_3O_{12}$ and $Yb_{0.2}Dy_{1.8}W_3O_{12}$ are shown in Fig. 1(a) and (b). The lattice parameters of $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$) are shown in Fig. 2 and it is noted that the lattice parameters *a*, *b*, *c* and cell volume *V* increase with the Dy content increasing as expected because the ionic size of Dy^{3+} (91 pm) is larger than that of the Yb^{3+} (86 pm).

3.2. Thermal expansion by high temperature X-ray diffraction

The hygroscopic phenomenon is observed from room temperature XRD patterns of $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$), and the water molecules can change the thermal expansion property [11].

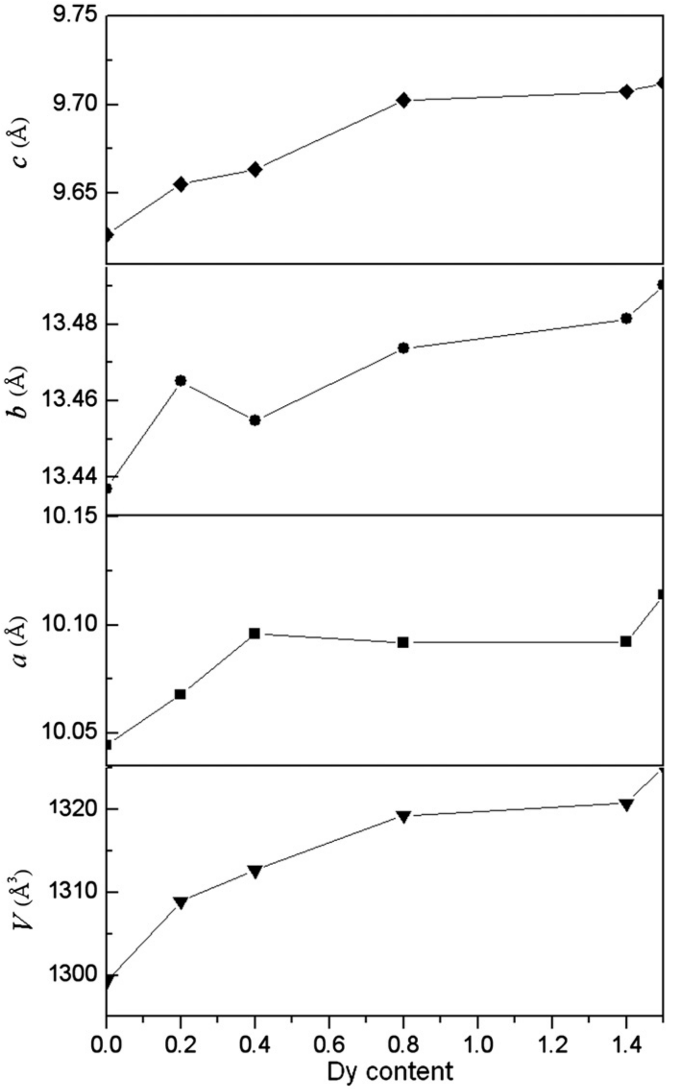

Fig. 2. The lattice parameters of $Yb_{2-x}Dy_xW_3O_{12}$ ($0\le x\le 1.5$) changing with the content of dysprosium.

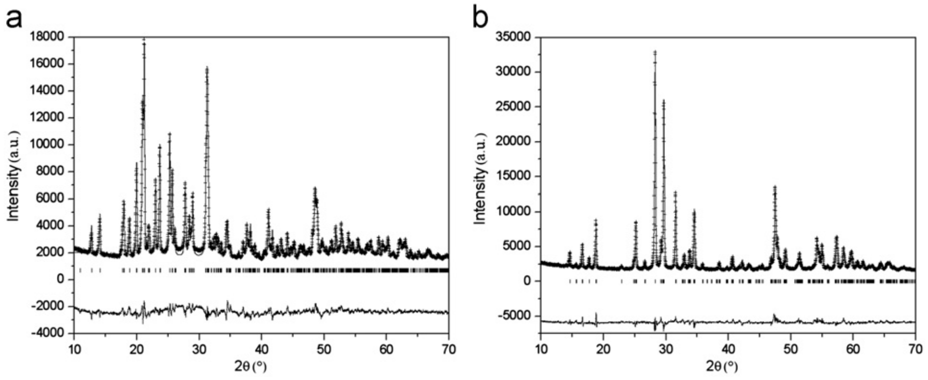

Fig. 1. (a) Observed (+), calculated (line) and difference profiles for the X-ray. Rietveld refinement of X-ray diffraction pattern of $Yb_{1.2}Dy_{0.8}W_3O_{12}$ at 200 °C. Vertical bars indicate the position of Bragg peaks for the structure (*Rp* is 5.22% and *wRp* is 6.86%). (b) Observed (+), calculated (line) and difference profiles for the X-ray. Rietveld refinement of X-ray diffraction pattern of $Yb_{0.2}Dy_{1.8}W_3O_{12}$ at 200 °C. Vertical bars indicate the position of Bragg peaks for the structure (*Rp* is 4.21% and *wRp* is 5.33%).