

# Synthesis and negative thermal expansion properties of solid solutions $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$ ( $0 \leq x \leq 2$ )

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## Abstract

A new series of rare earth solid solutions  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  were successfully synthesized by the solid-state method. Effects of substituted ion lanthanum on the microstructures and thermal expansion properties in the resulting  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ceramics were investigated by X-ray diffraction (XRD), thermogravimetric analyzer (TGA), field emission scanning electron microscope (FESEM) and thermal mechanical analyzer (TMA). Results indicate that the structural phase transition of the  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  changes from orthorhombic to monoclinic with increasing substituted content of lanthanum. The pure phases can form in the composition range of  $0 \leq x < 0.5$  with orthorhombic structure and  $1.5 < x \leq 2$  with monoclinic one. High lanthanum content leads to a low hygroscopicity of  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$ . Negative thermal coefficients of the  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $0 \leq x \leq 2$ ) also vary from  $-7.78 \times 10^{-6} \text{ K}^{-1}$  to  $2.06 \times 10^{-6} \text{ K}^{-1}$  with increasing substituted content of lanthanum.

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## 1. Introduction

Thermal expansion is one of the properties which must be considered in the application of highly functional materials because the mismatch of thermal expansion between component materials can cause problems, such as mechanical destruction and positional deviation, in electrical, optical and high-temperature devices. One of the possible methods that can solve these problems is preparing materials with controllable or near-zero expansion coefficients. A simple idea to prepare them is combining negative thermal expansion (NTE) materials with positive thermal expansion materials [1–6].

Recently, the family  $\text{A}_2\text{W}_3\text{O}_{12}$  materials have attracted widespread interest due to their larruping thermal expansion properties. The thermal expansion coefficients of  $\text{A}_2\text{W}_3\text{O}_{12}$  can be tailored to be positive or negative by changing the A cation. Some compounds of the type  $\text{A}_2\text{W}_3\text{O}_{12}$  materials have been reported. It has been found that there are two structures in the family  $\text{A}_2\text{W}_3\text{O}_{12}$  compounds, orthorhombic and monoclinic, and

thermal expansion properties are mainly related to the structures. Compounds with orthorhombic structure exhibit negative thermal expansion, such as  $\text{Sc}_2\text{W}_3\text{O}_{12}$  [7,8],  $\text{Y}_2\text{W}_3\text{O}_{12}$  [9,10],  $\text{Er}_2\text{W}_3\text{O}_{12}$  [10,11] and  $\text{Lu}_2\text{W}_3\text{O}_{12}$  [12], this orthorhombic structure is composed of corner-shared  $\text{AO}_6$  octahedra and  $\text{WO}_4$  tetrahedra. A–O–W linkages in their structure can accommodate transverse thermal vibrations and lead to the NTE [13]. Compounds with monoclinic structure exhibit positive thermal expansion, such as  $\text{La}_2\text{W}_3\text{O}_{12}$  [10],  $\text{Dy}_2\text{W}_3\text{O}_{12}$  [10], and  $\text{Nd}_2\text{W}_3\text{O}_{12}$  [10], this monoclinic structure is composed of edge-sharing  $\text{AO}_8$  polyhedra and  $\text{WO}_4$  tetrahedra.

It is reported that controllable thermal expansion coefficient in  $\text{A}_2\text{W}_3\text{O}_{12}$  may be obtained by partial chemical substitution of the “A” cation by another trivalent cation [1,14–17].  $\text{Yb}_2\text{W}_3\text{O}_{12}$  crystallizes in an orthorhombic symmetry (*Pnca*) and exhibits NTE with the linear thermal expansion coefficient of  $-9.65 \times 10^{-6} \text{ K}^{-1}$  in the temperature range from 373 K to 873 K [10,11]. Whereas,  $\text{La}_2\text{W}_3\text{O}_{12}$  crystallizes in a monoclinic symmetry (*C2/c*) and exhibits positive thermal expansion with the linear thermal expansion coefficient of  $4.14 \times 10^{-6} \text{ K}^{-1}$  in the temperature range from room temperature to 1073 K [10]. It is therefore possible to obtain the solid solutions  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  with controllable thermal expansion coefficient by

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partial substitution of  $\text{Yb}^{3+}$  with  $\text{La}^{3+}$ , and control the thermal expansion coefficient to be negative, positive and even zero by careful adjustment of the Yb/La ration.

In this paper, a series of  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $0 \leq x \leq 2$ ) ceramics were successfully prepared by solid-state reaction and the effects of substituted lanthanum content on the microstructure and thermal expansion were also studied.

## 2. Experimental

### 2.1. Preparation of the $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$ ( $0 \leq x \leq 2$ ) samples

All the  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $0 \leq x \leq 2$ ) solid solutions were synthesized by the conventional solid-state reaction method from the corresponding oxides  $\text{Yb}_2\text{O}_3$  (purity  $\geq 99.9\%$ ),  $\text{La}_2\text{O}_3$  (purity  $\geq 99.5\%$ ) and  $\text{WO}_3$  (purity  $\geq 99.5\%$ ). All the starting materials were preheated at  $300^\circ\text{C}$  for 24 h before weighting to protect from  $\text{H}_2\text{O}$ . Stoichiometric ratios of the reactants were fully ground together and then pressed into pellets. The pellets were calcined at  $1000^\circ\text{C}$  in air for 24 h with an intermediate regrinding.

### 2.2. Experimental techniques

The resulting samples were characterized by powder X-ray diffraction (XRD) using Cu K $\alpha$  radiation ( $\lambda = 0.15418\text{ nm}$ ) with 40 kV/200 mA (D/max2500, Rigaku). The XRD data were collected with a scanning speed of  $5^\circ (2\theta)/\text{min}$  in the  $2\theta$  range from  $10^\circ$  to  $40^\circ$  by continuum scanning method. The thermogravimetric curves of the samples were collected in the open air from room temperature to  $300^\circ\text{C}$  using thermogravimetric analyzer (TGA, Pyris1). The heating rate is  $10^\circ\text{C}/\text{min}$ . The microstructures of the samples were observed by a field emission scanning electron microscope (FESEM, Hitachi S-4800) under an acceleration voltage of 15 kV. Densities of the samples were measured using Archimedes' method. The thermal expansion coefficients of the samples were measured by thermal mechanical analyzer (TMA/SS, Seiko 6300). The measurements were carried out at the rate of  $10^\circ\text{C}/\text{min}$  in the open air from room temperature to  $700^\circ\text{C}$ .

## 3. Results and discussion

### 3.1. XRD analysis

Phase identifications of compounds  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  were carried out by X-ray powder diffraction. Fig. 1 shows the typical XRD patterns of the obtained  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) ceramics. Owing to the difference between  $\text{Yb}_2\text{W}_3\text{O}_{12}$  (monoclinic,  $C2/c$ ) and  $\text{La}_2\text{W}_3\text{O}_{12}$  (orthorhombic,  $Pnca$ ) in their structures and their cation radius, solid solutions  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  only can form in certain composition range by solid state reaction. As one can see in Fig. 1, the  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 1.5, 1.75, 2$ ) synthesized with different amount of lanthanum have almost the same XRD patterns, and all the peak positions of

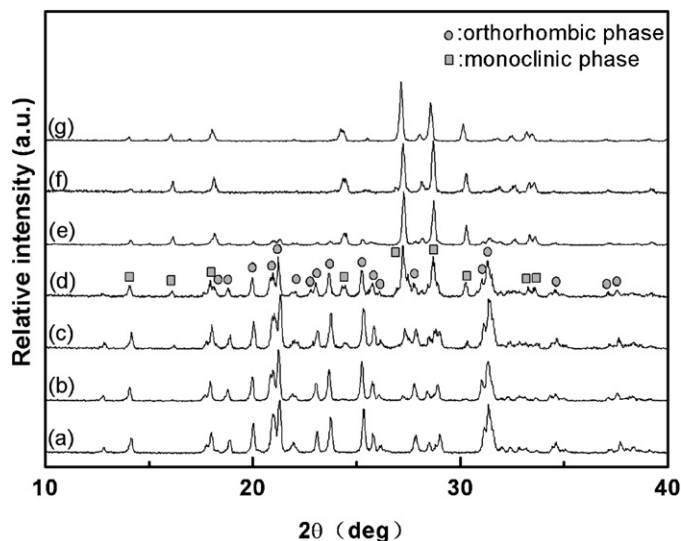


Fig. 1. XRD patterns of the obtained  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$ ) ceramics (a)  $\text{Yb}_2\text{W}_3\text{O}_{12}$ ; (b)  $\text{Yb}_{1.75}\text{La}_{0.25}\text{W}_3\text{O}_{12}$ ; (c)  $\text{Yb}_{1.5}\text{La}_{0.5}\text{W}_3\text{O}_{12}$ ; (d)  $\text{Yb}_1\text{La}_1\text{W}_3\text{O}_{12}$ ; (e)  $\text{Yb}_{0.5}\text{La}_{1.5}\text{W}_3\text{O}_{12}$ ; (f)  $\text{Yb}_{0.25}\text{La}_{1.75}\text{W}_3\text{O}_{12}$ ; (g)  $\text{La}_2\text{W}_3\text{O}_{12}$ .

these samples are well indexed to the  $\text{La}_2\text{W}_3\text{O}_{12}$  (JCPDS 15-0438) except  $\text{Yb}_{0.5}\text{La}_{1.5}\text{W}_3\text{O}_{12}$ , several little peaks ascribed to  $\text{Yb}_2\text{W}_3\text{O}_{12}$  can be seen in Fig. 1(e), indicating pure phase of  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  can form in the composition range of  $1.5 < x \leq 2$  with monoclinic structure. Comparing with the XRD patterns of the  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 1.5, 1.75, 2$ ), it is found that all the diffraction angles shift towards higher  $2\theta$  angles with the increase of the amount of ytterbium ions, which can be obviously seen in Fig. 2. The refined cell parameters and volumes of  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 1.6, 1.7, 1.8, 1.9, 2$ ) were also measured by XRD and then calculated by Powder X software. As shown in Fig. 3, it can be seen that the lattice parameters  $a$ – $c$  and  $V$  increase gradually with the increasing lanthanum content owing to the ionic radii of  $\text{La}^{3+}$  (106.1 pm) is larger than that of  $\text{Yb}^{3+}$  (85.8 pm). This is in good agreement with the Vegard's law, and

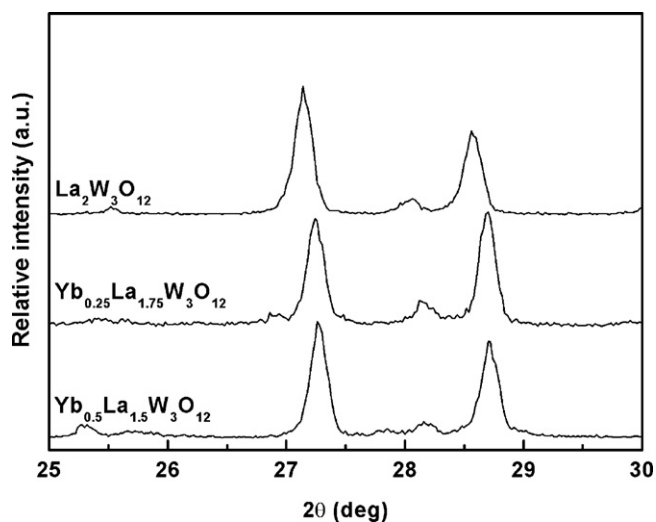


Fig. 2. Part XRD patterns of the obtained  $\text{Yb}_{2-x}\text{La}_x\text{W}_3\text{O}_{12}$  ( $x = 1.5, 1.75, 2$ ) ceramics.

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