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Synthesis and negative thermal expansion property of $Y_{2-x}La_xW_3O_{12}$ ($0 \leq x \leq 2$)

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Abstract

$Y_{2-x}La_xW_3O_{12}$ solid solutions were successfully synthesized by the solid state reaction method. The microstructure, hygroscopicity and thermal expansion property of the resulting samples were investigated by X-ray diffraction (XRD), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and thermal mechanical analysis (TMA). Results indicate that the structural phase transition of the $Y_{2-x}La_xW_3O_{12}$ changes from orthorhombic to monoclinic with increasing substituted content of lanthanum. The pure phase can form for $0 \leq x \leq 0.4$ with orthorhombic structure and for $1.5 \leq x \leq 2$ with monoclinic one. High lanthanum content leads to a low relative density of $Y_{2-x}La_xW_3O_{12}$ ceramic. Thermal expansion coefficients of the $Y_{2-x}La_xW_3O_{12}$ ($0 \leq x \leq 2$) ceramics also vary from $-9.59 \times 10^{-6}\,K^{-1}$ to $2.06 \times 10^{-6}\,K^{-1}$ with increasing substituted content of lanthanum. The obtained $Y_{0.25}La_{1.75}W_3O_{12}$ ceramic shows almost zero thermal expansion and its average linear thermal expansion coefficient is $-0.66 \times 10^{-6}\,K^{-1}$ from 103 °C to 700 °C.

Keywords: B. Composites; C. Thermal expansion; D. Ceramics ; Tungstates

1. Introduction

Thermal expansion is generally considered to be an important property 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 coefficient. Recently, negative thermal expansion (NTE) materials have attracted widespread interests due to their potential applications in controllable thermal expansion composites and coatings. We can combine the negative thermal expansion materials with positive thermal expansion materials to form various materials with controllable thermal expansion, being positive, negative or even zero.

Much attention has been recently paid to the materials with the general formula $A_2W_3O_{12}$ owing to their interesting physical and chemical properties. It has been found that there are two structures in the family of $A_2W_3O_{12}$ compounds, orthorhombic and monoclinic, and the thermal expansion property is mainly related to the exact structure of the compound [1]. Compounds with orthorhombic structures exhibit negative thermal expansion, such as $Sc_2W_3O_{12}$ [3,4], $Y_2W_3O_{12}$ [1,5,6], $Er_2W_3O_{12}$ [1,7] and $Lu_2W_3O_{12}$ [8], this orthorhombic structure is composed of corner-shared AO_6 octahedra and WO_4 tetrahedra. A–O–W linkages in their structures can accommodate transverse thermal vibrations and lead to the NTE [6]. Compounds with monoclinic structures exhibit positive thermal expansion, such as $La_2W_3O_{12}$ [1,2], $Dy_2W_3O_{12}$ [1], and $Nd_2W_3O_{12}$ [1], this monoclinic structure is composed of edge-sharing AO_8 polyhedra and WO_4 tetrahedra.

It is reported that controllable thermal expansion coefficient in $A_2W_3O_{12}$ may be obtained by partial chemical substitution of the A cation by another trivalent cation [9–13]. $Y_2W_3O_{12}$ crystallizes in an orthorhombic symmetry

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(*Pnca*) and exhibits NTE with the linear thermal expansion coefficient of $-8.35\times10^{-6}\,K^{-1}$ in the temperature range from 300 K to 1100 K [14]. However, $La_2W_3O_{12}$ crystallizes in a monoclinic symmetry ($C2/c$) and exhibits positive thermal expansion with the linear thermal expansion coefficient of $4.14\times10^{-6}\,K^{-1}$ in the temperature range from room temperature to 1073 K [1]. It is therefore possible to obtain the $Y_{2-x}La_xW_3O_{12}$ ceramic with controllable thermal expansion coefficient by partial substitution of Y^{3+} with La^{3+}, and control the thermal expansion coefficient to be negative, positive and even zero by careful adjustment of the Y/La ratio. Here in this report, a new series of $Y_{2-x}La_xW_3O_{12}$ ($0\leq x\leq2$) ceramics was successfully prepared by the solid state reaction method and the effects of substituted lanthanum content on the microstructure, density, hygroscopicity and thermal expansion property were also studied.

2. Experimental

2.1. Preparation of the $Y_{2-x}La_xW_3O_{12}$ ($0\leq x\leq2$) samples

The samples of $Y_{2-x}La_xW_3O_{12}$ ($0\leq x\leq2$) ceramics were prepared by the conventional solid state reaction method. Starting materials were Y_2O_3 (purity ≥ 99.9%), La_2O_3 (purity ≥ 99.5%) and WO_3 (purity ≥ 99.5%). All the starting materials were pre heated at 300 °C for 24 h before weighting to protect from H_2O. Stoichiometric ratios of the reactants were milled for 10 h to form a uniform mixture and dried at 90 °C, and then the mixtures were pre-calcined at 600 °C for 10 h. After pre-sintering, the mixtures were pressed into pellets (10 mm diameter and 2.5 mm height), and finally calcined at 1050 °C in air for 10 h.

2.2. Experimental techniques

The resulting samples were characterized by powder X-ray diffraction (XRD) using Cu Kα radiation ($\lambda=0.15418$ nm) with 40 kV/20 mA (D/max2500, Rigaku). The XRD data were collected with a scanning speed of 5° (2θ) per minute in the 2θ range from 10° to 50° by the continuum scanning method. The thermogravimetric curves of the samples were collected in the open air from room temperature to 300 °C using thermogravimetric analysis (TGA, Pyris1). The heating rate was 10 °C/ min. The microstructures of the samples were observed by a field emission scanning electron microscopy (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 °C/min in the open air from room temperature to 700 °C.

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows the typical XRD patterns of the obtained $Y_{2-x}La_xW_3O_{12}$ ($x=0$, 0.4, 0.5, 1, 1.5, 1.75, and 2) samples. As one can see in Fig. 1(e), (f) and (g), the $Y_{2-x}La_xW_3O_{12}$ ($x=1.5$, 1.75, and 2) samples, synthesized with different amount of lanthanum, have almost the same XRD patterns, and all the peak positions of these samples are well indexed to the $La_2W_3O_{12}$ (JCPDS 15-0438), indicating pure phase of $Y_{2-x}La_xW_3O_{12}$ can form for $1.5\leq x\leq2$ with monoclinic $La_2W_3O_{12}$-type structure. However, the samples $Y_{2-x}La_xW_3O_{12}$ ($0.4<x<1.5$) are isolated as biphasic mixture, and they contain both monoclinic and orthorhombic phases, and some representative reflections of the two phases are labeled in Fig. 1(c) and (d). $Y_{2-x}La_xW_3O_{12}$ can also form pure phase for $0\leq x\leq0.4$ with orthorhombic $Y_2W_3O_{12}$–type structure. The XRD patterns of the $Y_{2-x}La_xW_3O_{12}$ ($x=0$, 0.4, 0.5) are similar to those reported for $Y_2W_3O_{12}\cdot nH_2O$, which is hygroscopic at room temperature [1,5,6,14]. The board humps in the XRD patterns indicate that some amorphous phase might form owing to the absorption of water molecules in the frame-structure.

Compared with the XRD patterns of the $Y_{2-x}La_xW_3O_{12}$ ($x=1.5$, 1.75, and 2), it is found that all the diffraction lines shift toward lower 2θ angles with the increase of lanthanum content, which can be obviously seen in Fig. 2. It indicates that the lattice parameters of $Y_{2-x}La_xW_3O_{12}$ ($x=1.5$, 1.75, 2) increase with increasing lanthanum content owing to that the ionic radii of La^{3+} (106.1 pm) is larger than that of Y^{3+} (90 pm). This is in good agreement with the Vegard's law, and on the other hand it proves that the $Y_{2-x}La_xW_3O_{12}$ ($1.5\leq x\leq2$) compounds have been successfully synthesized.

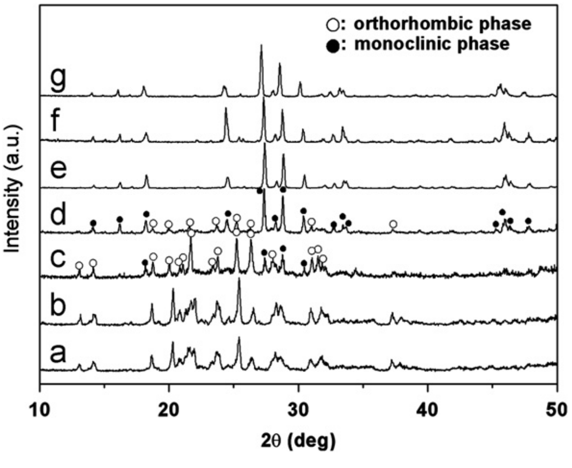

Fig. 1. XRD patterns of the obtained $Y_{2-x}La_xW_3O_{12}$ ($x=0$, 0.4, 0.5, 1, 1.5, 1.75, and 2) ceramics (a) $Y_2W_3O_{12}$, (b) $Y_{1.6}La_{0.4}W_3O_{12}$, (c) $Y_{1.5}La_{0.5}W_3O_{12}$, (d) $Y_1La_1W_3O_{12}$, (e) $Y_{0.5}La_{1.5}W_3O_{12}$, (f) $Y_{0.25}La_{1.75}W_3O_{12}$, and (g) $La_2W_3O_{12}$.