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Tailorable thermal expansion and hygroscopic properties of cerium-substituted $Y_2W_3O_{12}$ ceramics

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ABSTRACT

A new series of cerium-substituted $Y_2W_3O_{12}$ ceramics were first fabricated with the goal of tailoring the thermal expansion and reducing the hygroscopicity. Influence of cerium substitution on the structure, hygroscopicity and thermal expansion property of $Y_2W_3O_{12}$ ceramics were investigated using XRD, FESEM, HRTEM, XPS, TGA and TMA. Results indicate that the Y^{3+} can partly be substituted by Ce^{3+} in $Y_{2-x}Ce_xW_3O_{12}$ ceramics and increasing substitution of Y^{3+} in $Y_2W_3O_{12}$ by Ce^{3+} results in the crystal structure change from orthorhombic to monoclinic. Single-phase $Y_{2-x}Ce_xW_3O_{12}$ ceramics can be synthesized in the range of $0.0 \leq x \leq 0.25$ with an orthorhombic $Y_2W_3O_{12}$-type crystal structure and $1.0 < x \leq 2.0$ with monoclinic $Ce_2W_3O_{12}$-type crystal structure, respectively. As the amount of substituted cerium increases, the hygroscopic phenomenon of $Y_{2-x}Ce_xW_3O_{12}$ is significantly promoted, meanwhile the coefficient of thermal expansion gradually decreases. The linear coefficient of thermal expansion of $Y_{2-x}Ce_xW_3O_{12}$ ceramics can be adjusted from $-13.094 \times 10^{-6}\,K^{-1}$ to $2.327 \times 10^{-6}\,K^{-1}$ by changing the substituted amount of cerium. Moreover, $Y_{0.25}Ce_{1.75}W_3O_{12}$ does not absorb moisture in air and shows almost zero thermal expansion from 182 °C to 700 °C and its coefficient of thermal expansion is tested to be $-0.820 \times 10^{-6}\,K^{-1}$. This low thermal expansion $Y_{0.25}Ce_{1.75}W_3O_{12}$ material may have great potential applications in manufacturing precision device in many fields.

1. Introduction

As temperature rises, most solid materials will expand in nature. However, recently some materials have been found to show an opposite property. These materials shrink on heating and exhibit negative thermal expansion (NTE). NTE materials have attracted wide attention for their distinctive property and great application value. One of the applications is that the NTE materials can be mixed with the positive thermal expansion (PTE) materials, such as epoxy resin, metal and ceramics, to fabricate the composites with low or even zero coefficient of thermal expansion (CTE) [1–5]. Such functional materials will have a range of potential applications in microelectronic packaging and electronic, optical and high-temperature devices.

The series of $A_2M_3O_{12}$ materials, where A is trivalent transition metal cations or lanthanide and M is W^{6+} or Mo^{6+}, have aroused much attention for the last two decades. In terms of thermal expansion property, $A_2W_3O_{12}$ family is highly dependent on the type of A cation. When the A is a cation in the range from La to Eu, $A_2W_3O_{12}$ materials crystallize in monoclinic structure at room temperature and show PTE. While A is a cation in the range from Ho to Lu, $A_2W_3O_{12}$ materials will adopt an orthorhombic structure, which are highly hygroscopic in air and demonstrate a very intense NTE only after the loss of the hygroscopic water [6–12].

Furthermore, lager ionic radius of A cation leads to more negative thermal expansion in $A_2W_3O_{12}$ family. Thereby the presence of a larger sized A cation, such as Y^{3+}, in the structure of $A_2M_3O_{12}$ causes the most pronounced NTE over all known $A_2M_3O_{12}$ phases. This NTE property may be either isotropic or anisotropic. Thus, some materials show NTE in all three crystallographic directions, whereas others show this behavior in only one or two directions [13–17]. More remarkably, $Y_2W_3O_{12}$ exhibits NTE behavior along all three crystallographic directions, and consists of an open frame work with corner shared polyhedral [16,17]. NTE is

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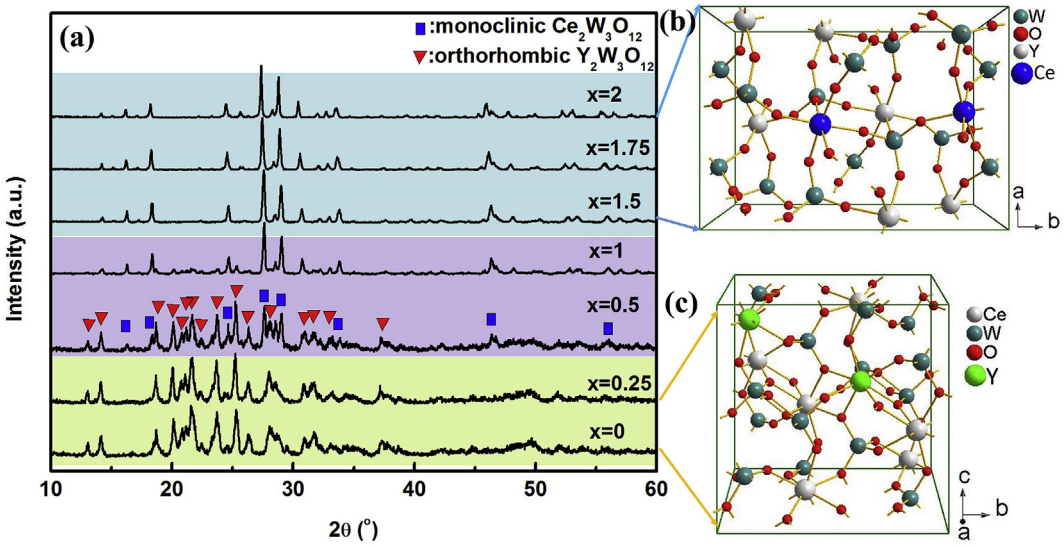

Fig. 1. Room temperature XRD patterns for the obtained $Y_{2-x}Ce_xW_3O_{12}$ ($0 \le x \le 2$) ceramics (a) and the crystal structures of $Y_{2-x}Ce_xW_3O_{12}$ (b) monoclinic (space group:*C*2/*c*) and (c) orthorhombic (space group: Pnca) forms.

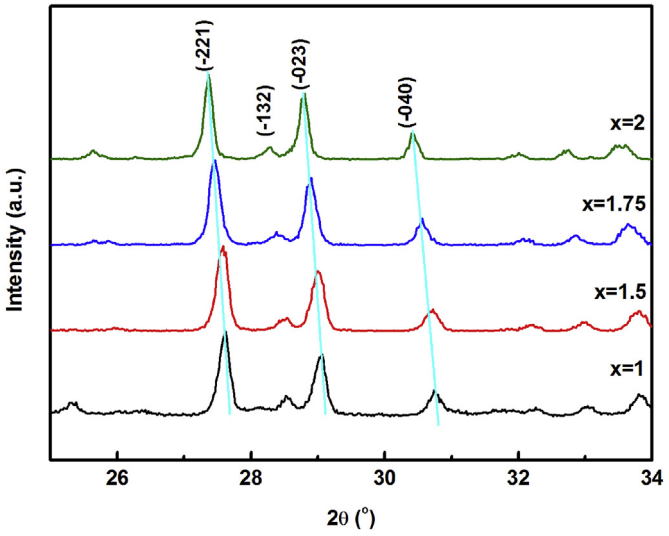

Fig. 2. Partial XRD patterns for $Y_{2-x}Ce_xW_3O_{12}$ ($x = 1, 1.5, 1.75, 2$) ceramics.

Table 1
The unit cell parameters of $Y_{2-x}Ce_xW_3O_{12}$ ($x = 1, 1.5, 1.75$ and 1) compounds as a function of composition.

$Y_{2-x}Ce_xW_3O_{12}$	a (Å)	b (Å)	c (Å)	β (°)	V(Å^3)
$x = 2$	7.833	11.745	11.720	109.36	1007.62
$x = 1.75$	7.800	11.690	11.690	109.44	995.68
$x = 1.5$	7.779	11.645	11.645	109.47	985.28
$x = 1$	7.765	11.613	11.613	109.50	978.97

attributed to the transverse thermal vibrations of bridging-O atoms of A-O-W linkages in their structure [6].

It has reported that partial substitution of the A-site cation may dramatically influence the CET of $A_2M_3O_{12}$ [11,12,18,19]. Non-hygroscopic $Ce_2W_3O_{12}$ crystallizes in monoclinic structure and exhibits PTE. In this work, an attempt has been made to prepare $Y_{2-x}Ce_xW_3O_{12}$ solid solutions with controllable CET and overcome the hygroscopicity of $Y_2W_3O_{12}$. Essentially, this work aims to adjust the CTE of $Y_{2-x}Ce_xW_3O_{12}$ to be negative, near-zero and positive by changing the Y/Ce ration. The influence of substituted Ce^{3+} on the crystal structure, hygroscopicity and the CTE value of $Y_{2-x}Ce_xW_3O_{12}$ ($0 \le x \le 2$) ceramics was also studied.

2. Experimental

Analytically pure Y_2O_3, CeO_2 and WO_3 powders were used as raw materials to prepare $Y_{2-x}Ce_xW_3O_{12}$ ($0 \le x \le 2$) ceramics. All the raw materials were preheated at 500 °C for 12 h and then weighed in accordance with the different stoichiometry. Powder mixture was co-milled for 12 h in alcohol and dried at 100 °C. Subsequently, the mixtures were heated at 600 °C for 6 h, followed by an intermediate grinding at room temperature and then pressed into pellets at 25 MPa. Finally, the pellets were heated at 950 °C for 12 h in the furnace.

Phase composition was characterized using a powder X-ray diffractometer (XRD, Shimadzu-7000) with CuKα incident radiation at 40 kV and 30 mA. The data was collected in the 2θ angular range of 10°–60° with a scanning speed of 5°/min. The micromorphology of the specimen was studied using a scanning electron microscope (SEM, Hitachi S-4800). The microscopic observation and elemental mapping were also conducted using a FEI-Tecnai F30 S-TWIN high resolution transmission electron microscope (TEM) and an energy dispersive X-ray spectroscopy (EDX). The elemental electrovalence and compositions of the sample were carried out using a X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific ESCALAB250Xi). The hygroscopicity of the sample was measured using a thermogravimetric analyzer (TGA, Perkin-Elmer Pyris1) in the temperature range from room temperature to 300 °C with a heating rate of 10 °C/min. The thermal expansion behavior of the sample was characterized using a thermal mechanical analyzer (TMA, Seiko 6300), and the heating rate is 10 °C/min from room temperature to 700 °C.

3. Results and discussion

3.1. Phase identification

XRD patterns of $Y_{2-x}Ce_xW_3O_{12}$ ($x = 0, 0.25, 0.5, 1, 1.5, 1.75, 2$)