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Synthesis and tunable thermal expansion properties of $Sc_{2-x}Y_xW_3O_{12}$ solid solutions

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Abstract

A new series of rare earth solid solutions $Sc_{2-x}Y_xW_3O_{12}$ was successfully synthesized by the conventional solid-state method. Effects of doping ion yttrium on the crystal structure, morphology and thermal expansion property of as-prepared $Sc_{2-x}Y_xW_3O_{12}$ ceramics were investigated by X-ray diffraction (XRD), thermogravimetric analysis (TG), field emission scanning electron microscope (FE-SEM) and thermal mechanical analyzer (TMA). Results indicate that the obtained $Sc_{2-x}Y_xW_3O_{12}$ samples with Y doping of $0 \le x \le 0.5$ are in the form of orthorhombic $Sc_2W_3O_{12}$-structure and show negative thermal expansion (NTE) from room temperature to 600 °C; while as-synthesized materials with Y doping of $1.5 \le x \le 2$ take hygroscopic $Y_2W_3O_{12} \cdot nH_2O$-structure at room temperature and exhibit NTE only after losing water molecules. It is suggested that the obvious difference in crystal structure leads to different thermal expansion behaviors in $Sc_{2-x}Y_xW_3O_{12}$. Thus it is proposed that thermal expansion properties of $Sc_{2-x}Y_xW_3O_{12}$ can be adjusted by the employment of Y dopant; the obtained $Sc_{1.5}Y_{0.5}W_3O_{12}$ ceramic shows almost zero thermal expansion and its average linear thermal expansion coefficient is $-0.00683 \times 10^{-6}\,°C^{-1}$ in the 25–250 °C range.

Keywords: C. Thermal expansion; Tungstate; Solid solution; $Sc_{2-x}Y_xW_3O_{12}$

1. Introduction

Flexible negative thermal expansion (NTE) was reported in a large family of tungstate and molybdate with the general formula $A_2M_3O_{12}$, where A could be rare earth elements and M could be W or Mo [1–7]. It was reported by Forster et al. [8] that the magnitude of thermal expansion in this family is related to cation size. A^{3+}, with a wide range of radii from 0.67 Å (Al^{3+}) to 1.075 Å (Gd^{3+}), could be partially replaced by other rare earth elements (B^{3+}) to get $A_{2-x}B_x(W,Mo)_3O_{12}$ solid solutions. In theory, it offers an alternative way to adjust the thermal expansion coefficient (TEC) of $A_{2-x}B_x(W,Mo)_3O_{12}$ to any desired value including zero by varying the type and content of B [9,10].

Two typical structures, orthorhombic and monoclinic, are found in these tungstates; it is believed that thermal expansion properties of tungstates are mainly related to crystal structure of specific materials [4,6,9,11]. The orthorhombic structure has an open framework structure with A–O–W linkages, which can accommodate for transverse thermal vibrations required by negative thermal expansion. Monoclinic $A_2W_3O_{12}$ materials have an edge shared structure with densely-packed characteristic and cannot accommodate for transverse thermal vibrations.

$Sc_2W_3O_{12}$ with typical orthorhombic structure shows negative thermal expansion in a wide temperature range from 10 to 1200 K. Its NTE is considered to go on to its melting point of 1913 K. TECs of $Sc_2W_3O_{12}$ ceramics are in the range of -6 to $-11 \times 10^{-6}\,K^{-1}$ [1,12]. However, it is notable that, with the exception of $Sc_2W_3O_{12}$, the rest of $A_2W_3O_{12}$ materials with orthorhombic structure are highly hygroscopic and exhibit negative thermal expansion only after the complete removal of water molecules [5,6,12,13], for example $Y_2W_3O_{12}$ [4,5,9], $Lu_2W_3O_{12}$ [8], $Er_2W_3O_{12}$ [4,9,14,15], $Yb_2W_3O_{12}$ [5,15] and $Dy_2W_3O_{12}$ [16]. Among these tungstates, $Y_2W_3O_{12}$ has an huge bulk TEC of $-20.9 \times 10^{-6}\,K^{-1}$ for temperature range of 298–1073 K [5,17], thus it is highly desirable to investigate the change in tungstates' TECs when Sc^{3+}(radii 0.745 Å) is partially substituted with Y^{3+} (radii 0.89 Å) and to further demonstrate the controllable synthesis of $Sc_{2-x}Y_xW_3O_{12}$ solid

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solutions in the presence of different Sc/Y molar ratios. Herein, a new series of $Sc_{2-x}Y_xW_3O_{12}$ ($0 \le x \le 2$) solid solutions were synthesized by the solid state reaction; effects of doping yttrium content on crystal structure, hygroscopic, morphology and thermal expansion property were studied.

2. Experimental

2.1. Preparation of the $Sc_{2-x}Y_xW_3O_{12}$ ($0 \le x \le 2$) samples

$Sc_{2-x}Y_xW_3O_{12}$ samples were prepared by the conventional solid-state reaction from corresponding oxides Sc_2O_3 (99.9% purity), Y_2O_3 (99.5% purity) and WO_3 (99.0% purity). All starting materials were preheated at 300 °C for 24 h before weighting to protect from H_2O. Stoichiometric ratios of the reactants were fully ground together and then pressed into rectangular ceramic rods with length 15 mm and width 5 mm. The rods were calcined at 1000 °C in air for 18 h.

2.2. 0Characterization

The resulting samples were identified by X-ray powder diffraction (XRD) analysis (D/max-2500, Rigaku, Japan) using Cu-Kα radiation (λ=0.15406 nm) with 40 kV/200 mA. The XRD data were collected with a scan speed of 5° min^{-1} in the 2θ range from 10° to 50° by the continuum scanning method. The lattice parameters of samples were calculated by the Powder X software [18]. The thermogravimetric curves of the samples were collected in the open air from room temperature to 800 °C using thermogravimetric analysis (TG, Pyris1). The heating rate was 10 °C/min. Their microstructures were observed by Field emission scanning electron microscopy (FE-SEM, Joel 7000). Thermal expansion coefficients of samples in 30–600 °C were measured by WTD-2 model thermo dilatometer. The measurements were carried out at the rate of 10 °C/min in the open air from room temperature to 600 °C.

3. Results and discussion

3.1. 0XRD analysis

The typical XRD patterns of the obtained $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5, 1, 1.5, 1.75 and 2) samples are shown in Fig. 1(A). The $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) materials synthesized with different amounts of yttrium demonstrate almost the same XRD patterns and all peaks of these samples are well indexed to the orthorhombic $Sc_2W_3O_{12}$ (JCPDS No. 21-1065). It is indicated that pure phase of $Sc_{2-x}Y_xW_3O_{12}$ can form in the composition range of $0 \le x \le 0.5$ with orthorhombic structure. The XRD pattern of $ScYW_3O_{12}$ is very similar to that of orthorhombic $Sc_2W_3O_{12}$ while the diffraction peaks show obvious broadening, which might be caused by the lattice distortion due to the large number substitution of Y ion. The XRD patterns of samples with x=1.5, 1.75, 2 are almost the same as that reported in the literature for hygroscopic $Y_2W_3O_{12} \cdot nH_2O$ [5,17,19], implying that $Sc_{2-x}Y_xW_3O_{12}$ ($1.5 \le x \le 2$) materials adopt hygroscopic $Y_2W_3O_{12}$-type structure at room temperature.

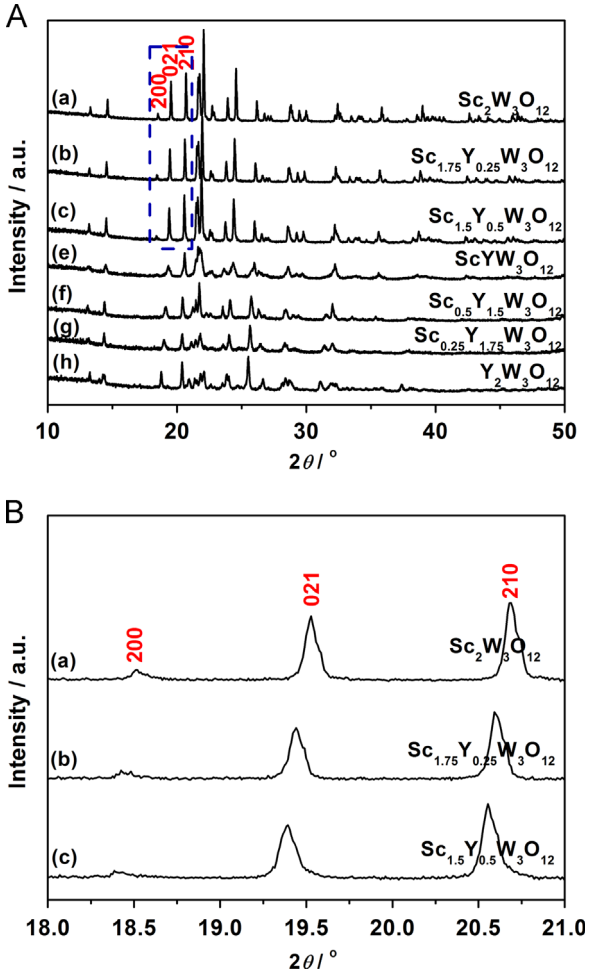

Fig. 1. (A) XRD patterns of the obtained $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5, 1, 1.5, 1.75 and 2) solid solutions and (B) partial enlarged XRD patterns of $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) solid solutions.

Table 1
Lattice parameters and volumes of $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) solid solutions.

Solid solutions	a/Å	b/Å	c/Å	V/Å^3
$Sc_2W_3O_{12}$	9.577	13.315	9.663	1232.48
$Sc_{1.75}Y_{0.25}W_3O_{12}$	9.582	13.389	9.684	1242.44
$Sc_{1.5}Y_{0.5}W_3O_{12}$	9.593	13.448	9.691	1249.43

Partial enlarged XRD patterns of $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) samples are shown in Fig. 1(B), it could be found that all diffraction lines shift toward lower 2θ angles with the increase in yttrium content. This phenomenon indicates that the lattice parameters of $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) increase with a higher percentage of yttrium dopant owing to that the ionic radii of Y^{3+} (0.89 Å) is larger than that of Sc^{3+} (0.745 Å). The calculated lattice parameters of $Sc_{2-x}Y_xW_3O_{12}$ (x=0, 0.25, 0.5) solid solutions at room temperature are given