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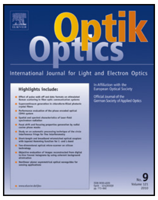

Short note

Near-zero thermal expansion of $Zr_xHf_{1\text{-}x}MgMo_3O_{12}$ in a larger temperature range

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ABSTRACT

$Zr_xHf_{1\text{-}x}MgMo_3O_{12}$ with $x = 0.3$, 0.5, 0.7 and 0.8 are developed with a simple solid state method. It is shown that $Zr_xHf_{1\text{-}x}MgMo_3O_{12}$ ($x = 0$–1)crystallizes in an orthorhombic symmetry with space group *Pnma* and exhibits zero-thermal expansion in a large temperature range, with the value of x ($x = 0.5$, $\alpha_l = -0.363 \times 10^{-6}\,K^{-1}$ from 80 K to 573 K by X-ray diffraction and $\alpha_l = -0.25 \times 10^{-6}\,K^{-1}$ from 273 K to 673 K by dilatometer). $Zr_xHf_{1\text{-}x}MgMo_3O_{12}$ with $x = 0.5$ remains the orthorhombic structure without phase transition or decomposition at least from 158 K to 673 K and is not hygroscopic. These properties make it an excellent material with near-zero thermal expansion for a variety of applications.

1. Introduction

Since the discovery of isotropic negative thermal expansion (NTE) of ZrW_2O_8 in a wide temperature range (0.3 K–1050 K) [1], materials with NTE property have attracted much attention due to the possibility to design materials with desired and controllable coefficients of thermal expansion (CTE) [2–12]. Several families of materials have been found to exhibit NTE property, such as aluminate or tungstate, manganese nitrogen compounds doped with germanium, cyanides and fluorides [2].

Among the NTE materials, the $A_2M_3O_{12}$ family, where A is a trivalent cation and M is either Mo^{6+} or W^{6+}, exhibit NTE over wide temperature ranges due to the flexible open framework structure [3,4]. It was found that the two A^{3+} cations could be replaced by a combination of tetravalent and bivalent cations or one of A^{3+} cations was replaced by a tetravalent cation with one of the M^{6+} being replaced by a pentavalent cation [5,6]. With such substitutions, a series of new members of NTE materials including $HfMgW_3O_{12}$, $HfMgMo_3O_{12}$ and $ZrMgMo_3O_{12}$ have been developed [13–15]. Very recently, it was reported that substitution of W by Mo in $HfMgW_3O_{12}$ could alter the thermal expansion property greatly, making $HfMgW_{2.5}Mo_{0.5}O_{12}$ a zero thermal expansion and the coefficient of NTE in $HfMgW_{1.5}Mo_{1.5}O_{12}$ more than doubled with

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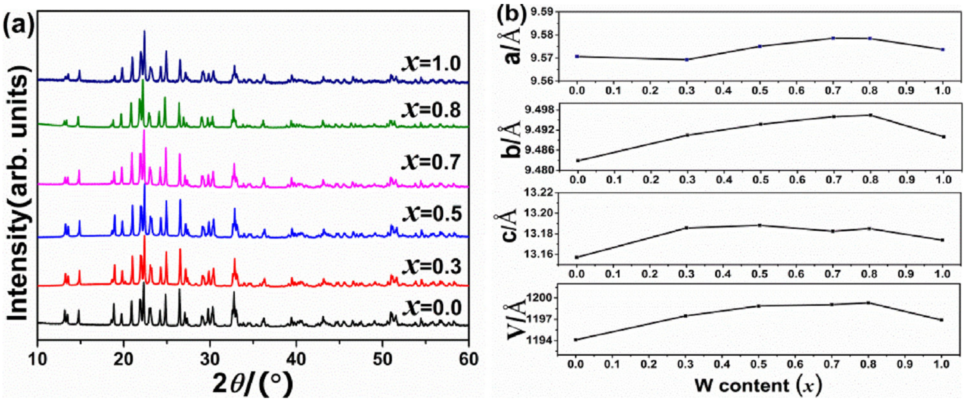

Fig. 1. (a) XRD patterns of $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.0$, 0.3, 0.5, 0.7, 0.8 and 1.0. For comparison, the XRD patterns of $ZrMgMo_3O_{12}$ and $HfMgMo_3O_{12}$ are also presented. (b) Lattice constants and volume change of $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.0$, 0.3, 0.5, 0.7, 0.8, 1.0.

respect to $HfMgW_3O_{12}$, though $HfMgMo_3O_{12}$ has a positive CTE [7]. Nevertheless, it is more desirable to develop materials with tailorable or near-zero thermal expansion properties in a single phase which is especially important to avoid interface thermal stress across a wide temperature range.

$HfMgMo_3O_{12}$ and $ZrMgMo_3O_{12}$ have low positive and negative CTEs, respectively. In the letter, we report the thermal expansion, phase transition and vibrational properties of single phase solid solutions of $Zr_xHf_{1-x}MgMo_3O_{12}$ with the aim to achieve zero expansion and to study the effect of the Zr(Hf) position substitution on the thermal expansion properties.

2. Experimental

The material of $Zr_xHf_{1-x}MgMo_3O_{12}$ was synthesized by solid state reactions. Analytical grade reagents of ZrO_2, HfO_2, MgO, MoO_3 were used as raw materials, which were weighted and ground according to the molar ratios of the destination materials $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.3$, 0.5, 0.7 and 0.8. The mixed powders were pressed into pellets by cold pressing under 200 MPa. The pressed pellets were sintered at 1023 K–1273 K for 4 h in a muffle furnace in air and cooled down to 300 K naturally.

Variable-temperature X-ray powder data were collected on a Rigaku (Japan, SmartLab 3 KW) diffractometer with Cu Kα ($\lambda = 0.15405$ nm) radiation. The temperature was controlled with a scan speed of 10 K/min in the 2θ range from 10° to 80°. Variable-temperature/RT Raman spectra were recorded with A LabRAM HR Evolution Raman spectrometer (France HORIBA JobinYvon S.A.A.) equipped with a Linkam THMS600 Heating and Freezing Stage (Japan Hightech) (an accuracy of ±0.1 K). The excitation wavelength is 633 nm and low excitation laser power is necessary to avoid local heating by the laser. The crystal constants were obtained by the POWDERX. The relative length change with temperature was measured with a dilatometer of Germany LINSEIS DIL L75.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.3$, 0.5, 0.7 and 0.8 at room temperature. It was reported that $HfMgMo_3O_{12}$ and $ZrMgMo_3O_{12}$ crystallizes in an orthorhombic structure with space group *Pnma* [13,14]. There are not obvious changes in the XRD patterns with increasing the content of Zr. This indicated that $Zr_xHf_{1-x}MgMo_3O_{12}$ could be identified as an orthorhombic structure with space group *Pnma* [13–18]. Fig. 1(b) shows the lattice constants and volume for x (0.0–1.0). It is evident that the lattice constants a and b increase with the contents of Zr but the c-axis changes very little. The reason of result is that the ion radius of Zr (72 pm) is larger than that of Hf (71 pm).

The relative length changes of $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.3$, 0.5, 0.7 and 0.8 were measured with a dilatometer (Fig. 2). It is found that all the samples of $Zr_xHf_{1-x}MgMo_3O_{12}$ with $x = 0.3$, 0.5, 0.7 and 0.8 present low thermal expansion or NTE property. The linear CTEs of $Zr_{0.3}Hf_{0.5}MgMo_3O_{12}$, $Zr_{0.5}Hf_{0.5}MgMo_3O_{12}$, $Zr_{0.7}Hf_{0.5}MgMo_3O_{12}$ and $Zr_{0.8}Hf_{0.2}MgMo_3O_{12}$ are about $-0.25 \times 10^{-6}\ K^{-1}$ (273 K– 673 K), $-0.25 \times 10^{-6}\ K^{-1}$ (273 K–673 K), $-0.125 \times 10^{-6}\ K^{-1}$ (273 K–673 K) and $-0.125 \times 10^{-6}\ K^{-1}$ (273 K–673 K), respectively. The abrupt change in the relative length curves suggests a phase transition of the materials.

Structure analysis was performed by the Pawley fit of the 297 K XRD pattern. Fig. 3 shows the results of $Zr_{0.5}Hf_{0.5}MgMo_3O_{12}$ at 297 K. It is shown that $Zr_{0.5}Hf_{0.5}MgMo_3O_{12}$ adopts an orthorhombic structure with space group *Pnma* (No. 62) and with acceptable values of Rexp = 3.83%, Rwp = 7.61%, and Rp = 5.78%. The lattice constants of $Zr_{0.5}Hf_{0.5}MgMo_3O_{12}$ are a = 9.5768 Å, b = 9.4897 Å, and c = 13.1818 Å, respectively. The samples for $x = 0.3$, 0.7, and 0.8 are analyzed with the same method. It is shown that they adopt the same orthorhombic and monoclinic structure at high and low temperature, respectively.

In order to see the intrinsic ZTE for $Zr_{0.5}Hf_{0.5}MgMo_3O_{12}$, we measured the XRD patterns of the sample at different temperatures and calculated lattice constants and volume at each temperature. Fig. 4(a) shows the selected temperature-dependent