Near-zero thermal expansion of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ with tailored phase transition*

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(Received 17 March 2016; revised manuscript received 11 April 2016; published online 25 June 2016)

Solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ are synthesized by solid state reaction with the aim to reduce the phase transition temperature of $In_2Mo_3O_{12}$ and improve its thermal expansion property. The effects of $(HfMg)^{6+}$ incorporation on the phase transition and thermal expansion are investigated. It is shown that the monoclinic-to-orthorhombic phase transition temperature obviously decreases and the coefficient of thermal expansion (CTE) of the orthorhombic becomes less negative and approaches to zero with increasing the content of $(HfMg)^{6+}$. A near zero thermal expansion covering the case at room temperature (RT) is achieved for the solid solutions with $x \geq 0.85$, implying potential applications of this material in many fields.

Keywords: phase transition, thermal expansion, thermal analysis, Raman spectrum

PACS: 61.50.Ks, 65.40.De, 64.60.–i, 78.30.–j **DOI:** 10.1088/1674-1056/25/8/086501

1. Introduction

The negative thermal expansion (NET) phenomena in some materials have received considerable attention in the past few years.[1–7] NTE materials have the promising potential applications in tailoring the coefficient of thermal expansion (CTE) of materials to reduce thermal stress.[3,8–10] However, a series of NTE materials such as $BiNiO_3$, $LaCu_3Fe_4O_{12}$, and Mn_3NX needs extreme synthesis conditions, like high pressure/temperature or exclusion of oxygen,[5,11–13] which restricts their applications in industry. Recently, some ceramics consisting of an open-framework with low thermal expansion or NTE[14–21] and low synthesis requirements, such as A_2O (A = Ag/Cu),[18] ABO_3 (A = Bi/Pb, B = Ni/Ti),[5] AMO_5 (A = Ta/Nb, M = V/P),[15,16] AM_2O_7 (A = Zr/Hf, M = V/P),[17] AM_2O_8 (A = Zr/Hf, M = Mo/W)[1] and $A_2M_3O_{12}$ (A is transition metal or rare earth, M is Mo or W) have been extensively investigated. The $A_2M_3O_{12}$ family is extremely attractive due to its chemical flexibility within the orthorhombic *Pbcn* (No. 60) space group, and it possesses a variation of linear CTE from low positive to large negative values.[22–32] This orthorhombic feature of $A_2M_3O_{12}$ makes it possible to be synthesized in solid solution state with controllable CTEs. Nevertheless, its heavy hygroscopicity[25–28] and abrupt change in thermal expansion property caused by phase transition from monoclinic to orthorhombic with increasing temperature[29–32] are still serious obstacles for practical applications of the $A_2M_3O_{12}$ family.

$In_2Mo_3O_{12}$ is a typical material of the $A_2M_3O_{12}$ family with the monoclinic-to-orthorhombic phase transition temperature of about 608 K to 610 K.[31] Miller *et al.*[30] reported an $In(HfMg)_{0.5}Mo_3O_{12}$ material and its monoclinic-to-orthorhombic structure transition occurring around 430 K. It means that the thermal expansion properties of $In_2Mo_3O_{12}$ and $In(HfMg)_{0.5}Mo_3O_{12}$ will be abruptly changed from giant positive to negative or near zero around their corresponding phase transition temperatures. The abrupt changes in thermal expansion deteriorate their mechanical properties and induce cracking, thus seriously hindering the applications of these materials. In order to reduce the phase transition temperature of $In_2Mo_3O_{12}$, Cr^{3+} was reported to be introduced into $In_2Mo_3O_{12}$,[32] but the phase transition temperature is still in a range of 523 K–673 K, which is much higher than room temperature (RT). It is because the phase transition (monoclinic-to-orthorhombic) temperature region of $Cr_2Mo_3O_{12}$ is as high as 623 K–673 K.[29] Reducing the phase transition temperature of $In_2Mo_3O_{12}$ to below room temperature (RT) and improving its thermal expansion property are still very attractive challenges.

In order to reduce the phase transition temperature of $In_2Mo_3O_{12}$, the most effective method is to partially replace In^{3+} with a larger trivalent ion such as Y^{3+} or Yb^{3+}. However, this may introduce crystal water at the same time such as

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11574276, 51302249, and 51503185) and the Doctoral Fund of the Ministry of Education of China (Grant No. 20114101110003).

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in the cases of $Yb_{2-x}Al_xMo_3O_{12}$[33] and $Fe_{2-x}Y_xMo_3O_{12}$.[27] Crystal water deteriorates the thermal expansion properties of materials because the releasing and admission of crystal water lead to serious expanding and contracting of the lattice during temperature circling. Besides, $HfMgMo_3O_{12}$ was shown to adopt an orthorhombic structure down to very low temperature.[34] It is expected that simultaneous doping with Hf^{4+} and Mg^{2+} into $In_2Mo_3O_{12}$ can not only reduce the phase transition temperature but also avoid introducing crystal water. At the same time, charge balance in the formula is maintained. In this paper, solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ are synthesized by solid state reaction in order to reduce the phase transition temperature of $In_2Mo_3O_{12}$ and improve its thermal expansion property. It is found that the phase transition temperature decreases as the amount of $(HfMg)^{6+}$ is increased and it is lower than RT when $x \geq 0.85$. With further increasing the amount of $(HfMg)^{6+}$, the near zero thermal expansion covering the case at RT is achieved so that the application scope of NTE materials can be further expanded.

2. Experiment

The starting materials of In_2O_3, MgO, HfO_2, and MoO_3 were mixed according to the mole ratios of the destination of materials of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ with $x = 0.0$, 0.1, 0.3, 0.5, 0.7, 0.75, 0.8, and 1.0. The mixtures were ground for 2 h in an agate mortar followed by sintering at 1073 K for 8 h in a furnace.

XRD measurements were carried out with a Bruker D8 Advance x-ray diffractometer. Raman spectra were recorded with a Renishaw inVia Raman spectrometer with 532-nm laser wavelength excitation. The differential scanning calorimeter (DSC) curves were obtained by the simultaneous thermal analyzer of Netzsch STA 449F3 in a temperature range of 298 K–673 K, under the 50 mL/min nitrogen (N_2) purge, with a heating rate of 10 K/min. The linear CTE was measured with a dilatometer of Linseis DIL L76 in an atmosphere environment and with a heating rate of 5 K/min.

3. Results and discussion

3.1. The phase transition through the introduction of $(HfMg)^{6+}$ component

Figure 1 shows the x-ray diffraction patterns of the $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ solid solutions when $x = 0$, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0. With increasing the amount of $(HfMg)^{6+}$ component, the diffraction peaks increase but shift first to higher degrees and then to lower degrees. The crystal structures can be identified as being monoclinic for $x \leq 0.7$ and orthorhombic for $x \geq 0.9$ from the XRD patterns.[22,31]

According to previous reports, the Raman spectra are sensitive to the monoclinic-to-orthorhombic phase transition.[27,35,36] In order to confirm the phase transition after the introduction of $(HfMg)^{6+}$, Raman spectra of the solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ are measured and shown in Fig. 2. The peak located at about 995 cm^{-1} originates from the monoclinic structure.[27,35,36] This Raman band decays gradually with increasing the content of $(HfMg)^{6+}$ and disappears finally at about $x = 0.85$, suggesting a transition from the monoclinic to orthorhombic phase occurring at this composition ratio.

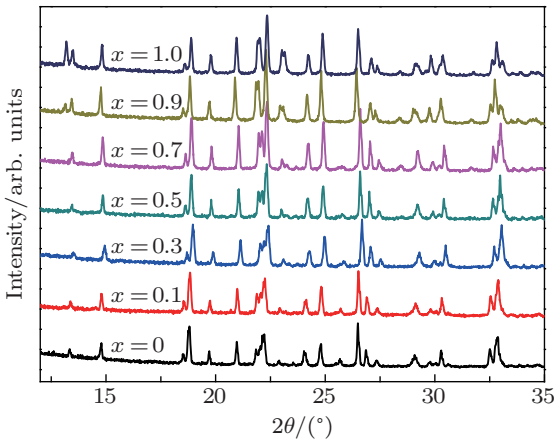


Fig. 1. (color online) The x-ray diffracion patterns of the solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$.

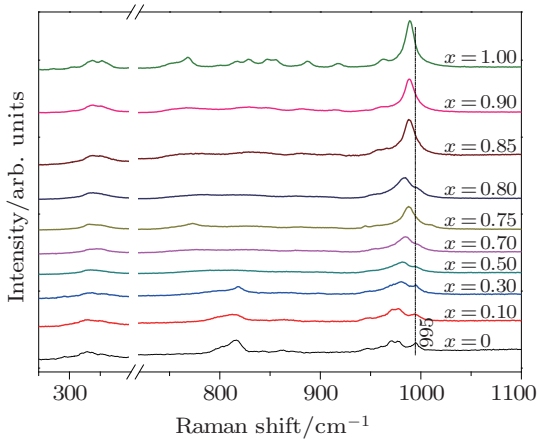


Fig. 2. (color online) The Raman spectra of the solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$.

3.2. Phase transition through increasing temperature

Figure 3(a) shows the DSC curves of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$. An endothermic peak appears at 616 K when $x = 0$, indicating the monoclinic-to-orthorhombic phase transition occurring at this temperature. The endothermic peak shifts to the lower temperature with increasing the amount of $(HfMg)^{6+}$. When $x = 0.5$, the endothermic peak appears at 425 K, which is close to the reported value of 430 K. With increasing the content of $(HfMg)^{6+}$, the endothermic peak becomes progressively weak so that the endothermic peak of the phase transition for $x \geq 0.7$ cannot be observed clearly as indicated by the arrow in Fig. 3(a). Through the fitting data for $x = 0$, 0.1, 0.3, and 0.5 as shown in Fig. 3(b), it can be de-

duced that a room-temperature orthorhombic phase requires $x \approx 0.84$. This accords well with the XRD and Raman results.

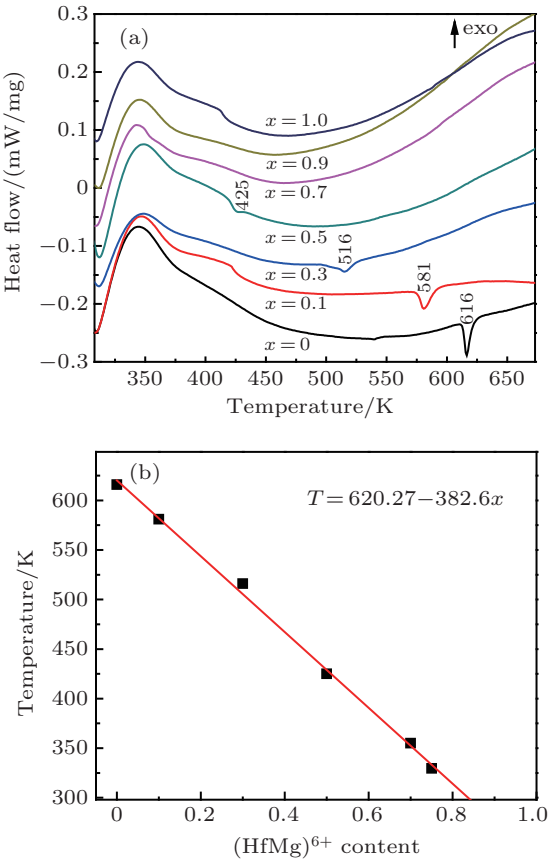


Fig. 3. (color online) (a) The DSC of the solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ and (b) linear fit and interpolation of the phase transition temperature vis $(HfMg)^{6+}$ content.

The progressively weakening and shifting to lower temperature of the endothermic peak indicate that the monoclinic-to-orthorhombic phase transition requires less energy with increasing the content of $(HfMg)^{6+}$, the physics behind which could be understood by the difference in electronegativity between $(HfMg)^{6+}$ and In^{3+}. The electronegativity values of Hf^{3+} (1.30) and Mg^{2+} (1.31) are smaller than that of In^{3+} (1.78). With increasing the content of $(HfMg)^{6+}$, the bridging oxygen connected with Hf^{4+} or Mg^{2+} gains more negative partial charge, which enhances the oxygen-oxygen repulsion force and makes the monoclinic-to-orthorhombic structure transition easier. When the sample with a higher content of $(HfMg)^{6+}$ is heated, its phase transition requires a lower temperature and less heat, resulting in the weakening and shifting of the endothermic peak.

3.3. Phase transition and near-zero thermal expansion

Figure 4 shows the variations of relative length of the $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ solid solutions with temperature. For $In_2Mo_3O_{12}$ ($x = 0.0$), its relative length increases slowly with temperature increasing from RT to 590 K, and then expands abruptly from 590 K to 623 K. The result indicates that the monoclinic-to-orthorhombic phase transition starts at about 590 K and ends at about 623 K, which is consistent with the phase transition temperature of the DSC result. The monoclinic-to-orthorhombic phase transition temperature decreases obviously with the increase of the amount of $(HfMg)^{6+}$, and the phase transition occurs at about 326 K for $x = 0.75$. The phase transition temperature even decreases to lower than RT when $x \geq 0.85$. It is worth noting that the CTEs of the orthorhombic phase become less negative and approach to zero with increasing the amount of $(HfMg)^{6+}$. A near zero thermal expansion for each of the solid solutions with $x \geq 0.8$ is achieved from RT to about 773 K.

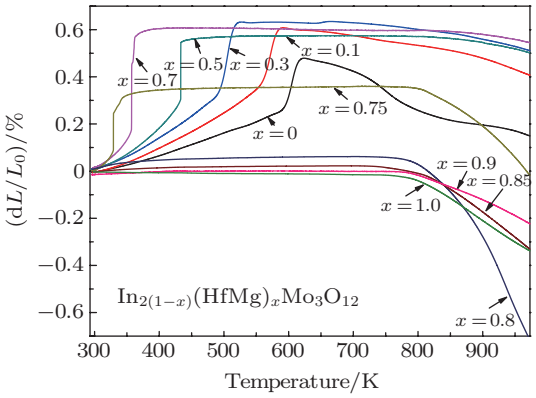


Fig. 4. (color online) Variations of relative length of the solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ with temperature.

The mechanisms for the near-zero CTE can be understood by the cation size effect of the six-coordinated In^{3+}, Hf^{4+}, and Mg^{2+} in the center of octahedron. As is well known, the NTE increases with a larger A^{3+} cation size for the $A_2M_3O_{12}$ family in the orthorhombic structure. The cation radius of In^{3+} is 0.080 nm while the average size of $(HfMg)^{6+}$ is 0.0715 nm. The In^{3+} cation size plays a decisive role for the NTE in $In_2Mo_3O_{12}$ above 623 K. However, with increasing the substitution amount of $(HfMg)^{6+}$ for In^{3+}, the NTE is reduced and even down to near-zero CTE due to the smaller average cation size. On the other hand, the thermal expansion of the $In(HfMg)_{0.5}M_3O_{12}$ is anisotropic,[30] the *a*- and *c*-axis contract while the *b*-axis expands on heating. The two factors result in the average thermal expansion of the cell volume approaching to zero.

4. Conclusions

Solid solutions of $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ are synthesized and the effects of $(HfMg)^{6+}$ incorporation on the phase transition and thermal expansion are investigated. It is shown that the monoclinic-to-orthorhombic phase transition temperature obviously decreases with increasing the content of $(HfMg)^{6+}$. The CTE of the orthorhombic structure becomes less negative and approaches to zero with increasing the content of $(HfMg)^{6+}$. A near zero thermal expansion over the range from RT to 773 K is achieved for the solid solutions

with $x \geq 0.8$. The $In_{2(1-x)}(HfMg)_xMo_3O_{12}$ solid solutions with near-zero thermal expansion property covering the case at RT hold great potential applications in many fields.

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