Near-Zero Thermal Expansion and Phase Transitions in HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$

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The effects of Zn$^{2+}$ incorporation on the phase formation, thermal expansion, phase transition, and vibrational properties of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ are investigated by XRD, dilatometry, and Raman spectroscopy. The results show that (i) single phase formation is only possible for $x \leq 0.5$, otherwise, additional phases of HfMo$_2$O$_8$ and ZnMoO$_4$ appear; (ii) The phase transition temperature from monoclinic to orthorhombic structure of the single phase HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ can be well-tailored, which increases with the content of Zn$^{2+}$; (iii) The incorporation of Zn$^{2+}$ leads to an pronounced reduction in the positive expansion of the $b$-axis and an enhanced negative thermal expansion (NTE) in the $c$-axes, leading to a near-zero thermal expansion (ZTE) property with lower anisotropy over a wide temperature range; (iv) Replacement of Mg$^{2+}$ by Zn$^{2+}$ weakens the Mo–O bonds as revealed by obvious red shifts of all the Mo–O stretching modes with increasing the content of Zn$^{2+}$ and improves the sintering performance of the samples which is observed by SEM. The mechanisms of the negative and near-ZTE are discussed.

Keywords: thermal expansion, near-zero thermal expansion, phase transition, X-ray diffraction (XRD), Raman spectrum

INTRODUCTION

Large difference in coefficients of thermal expansion (CTE) of materials could lead to performance deterioration and even failure of devices due to thermal stress when temperature changes abruptly or frequently. Since most materials expand on heating and contract on cooling, materials with opposite property, namely negative thermal expansion (NTE), are particularly desired for tailoring CTEs. The rediscovery of NTE in ZrW$_2$O$_8$ in a wide temperature range (Evans et al., 1996, 1997a) triggered continuous efforts on understanding the NTE phenomenon and searching for more NTE materials (Yang et al., 2007; Chen et al., 2013, 2015; Tallentire et al., 2013; Lama et al., 2014; Liu et al., 2014; Peng et al., 2014; Xiao et al., 2014; Hu et al., 2015). To date, different families of NTE materials based on various mechanisms, such as the phonon effect (Pryde et al., 1996; Wang et al., 2011; Bridges et al., 2014; Cheng et al., 2016a; Ge et al., 2016a), magnetovolume effect (Takenaka and Takagi, 2005; Qu et al., 2012; Yan et al., 2014), spontaneous ferroelectric polarization (Chen et al., 2013; Peng et al., 2016), and charge transfer (Long et al., 2009; Azuma et al., 2011; Yamada et al., 2016) have been reported. Among the materials, the family of A$_2$M$_3$O$_{12}$ (A = transition metal or a mixture of tetravalent and bivalent cations, M = W, Mo) have been particularly attractive, because whose NTEs go over a wide temperature range and can be tuned...
from low positive to large negative values due to chemical flexibility (Evans et al., 1997b; Suzuki and Omote, 2006; Wu et al., 2009, 2012, 2014; Li et al., 2011; Das et al., 2013; Miller et al., 2013; Song et al., 2014a; Liu et al., 2015; Chen et al., 2016; Cheng et al., 2016a).

In recent years, a number of novel NTE materials have been designed based on the basic structure of $\text{A}_2\text{M}_2\text{O}_{12}$ family, including those with a general formula $\text{ABM}_3\text{O}_{12}$ where $\text{A}$ is tetravalent $\text{Hf}^{4+}$ or $\text{Zr}^{4+}$ and $\text{B}$ is bivalent cation $\text{Mg}^{2+}$ or $\text{Mn}^{2+}$, and $\text{M}$ is $\text{W}$ or $\text{Mo}$ or a combination of them (Suzuki and Omote, 2004; Baiz et al., 2008; Gindhart et al., 2008; Marinkovic et al., 2008; Song et al., 2013; Li et al., 2016, 2017; Ge et al., 2016a; Liu et al., 2018) and those with a general formula $\text{AB}_2\text{XO}_{12}$ where $\text{A}$ and $\text{M}$ are the same as in $\text{ABM}_3\text{O}_{12}$, $\text{B}$ is a trivalent cation $\text{V}^{5+}$ or $\text{Cr}^{3+}$ transition metal group $\text{Pnma}(62)$ or $\text{Pna}_21$ (33) and transforms to monoclinic structure at 175 K (Miller et al., 2012).

In this paper, we investigate the effects of $\text{Zn}^{2+}$ incorporation on the structure, phase transition, thermal expansion, and vibrational properties of $\text{HfMgMo}_3\text{O}_{12}$. It is shown that single phase solid solution of $\text{HfMg}_{1-x}\text{Zn}_x\text{Mo}_3\text{O}_{12}$ can be achieved only for the compositions of $x \leq 0.5$, otherwise, additional phases of $\text{HfMo}_2\text{O}_8$ and $\text{ZnMoO}_4$ appear. The monoclinic to orthorhombic phase transition temperature increases with the content of $\text{Zn}^{2+}$ for $x \leq 0.5$ so that $\text{HfMg}_{0.5}\text{Zn}_{0.5}\text{Mo}_3\text{O}_{12}$ crystallizes in monoclinic phase and all other samples ($x \leq 0.4$) adopt orthorhombic structure at room temperature (RT). The incorporation of $\text{Zn}^{2+}$ alters the axial CTE differently for each axis and finally results in near-zero thermal expansion (ZTE) property over wide temperature ranges with smaller thermal expansion anisotropy with respect to $\text{HfMgMo}_3\text{O}_{12}$. The mechanisms of $\text{Zn}^{2+}$ incorporation on the phase transition, thermal expansion and vibrational properties are discussed.

**EXPERIMENTAL**

Analytic grade reagents of $\text{HfO}_2$, $\text{MgO}$, $\text{ZnO}$, and $\text{MoO}_3$ were mixed with stoichiometric ratios for $\text{HfMg}_{1-x}\text{Zn}_x\text{Mo}_3\text{O}_{12}$ with $x = 0.0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 1.0$. The mixtures were ground in an agate mortar for 2 h, then, pressed under 325 MPa into cylinders with diameter of 10 mm and height of 6 mm using a uniaxial tablet machine. The cylinders were sintered at 1,073 K for 5 h in a muffle furnace in air and cooled down to 300 K naturally.

The as-prepared samples were analyzed by XRD with a PANalytical X’Pert PRO X-ray Diffractometer to identify the crystalline phase. Variable-temperature X-ray powder data were collected on a Rigaku (Japan, SmartLab 3KW) diffractometer with Cu $K\alpha$ ($\lambda = 0.15405$ nm) radiation. Diffraction data were collected with a step size of 0.01° in the 2θ range of 10°–120°. The sample was heated at a rate of 10 K/min and remained at each measurement temperature for 5 min before measurement. Unit cell dimensions above the phase transition temperature were determined with software of PowderX. Variable-temperature/RT Raman spectra were recorded with a LabRAM HR Evolution Raman spectrometer (France HORIBA JobinYvon S.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 microstructures and energy dispersive spectra of the samples were examined with a scanning electron microscope (SEM, Model Quanta 250). The relative length changes were measured with LINSEIS DIL L75 dilatometer at the heating and cooling rates of 5 K/min.

**FIGURE 1** (A) X-ray diffraction patterns of the solid solutions of $\text{HfMg}_{1-x}\text{Zn}_x\text{Mo}_3\text{O}_{12}$; (B) Raman spectra of the solid solutions of $\text{HfMg}_{1-x}\text{Zn}_x\text{Mo}_3\text{O}_{12}$.
RESULTS AND DISCUSSION

Figure 1A shows the XRD patterns of the solid solutions of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$. When $x = 0.0$, the diffraction peaks are corresponding to HfMgMo$_3$O$_{12}$, which adopts an orthorhombic structure with space group $Pnma$ or $Pna2_1$ (Marinkovic et al., 2008). No obvious changes in the XRD patterns could be observed with increasing the content of Zn$^{2+}$ till $x = 0.4$. It is reasonable to conclude that HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ for $x \leq 0.4$ crystallized in an orthorhombic structure. Nevertheless, some subtle changes are observed for $x = 0.5$, such as the weak peak appearing at about 25.6$^\circ$ which is characteristic for a monoclinic structure (Song et al., 2014b; Ge et al., 2016a) of ABMo$_3$O$_{12}$. HfMg$_{0.5}$Zn$_{0.5}$Mo$_3$O$_{12}$ at RT is thus identified as a monoclinic structure. The XRD patterns change obviously with further increasing content of Zn$^{2+}$. Detailed analyses show that the newly appeared peaks correspond well to HfMo$_2$O$_8$ and ZnMoO$_4$ (Reichelt et al., 2000; Allen et al., 2004), respectively.

The above analysis is supported by Raman spectroscopic analysis (Figure 1B). The Raman spectra are consistent with each other for $x \leq 0.4$ while the Raman band at 988 cm$^{-1}$ splits into two bands at 980 and 998 cm$^{-1}$ for $x = 0.5$ (as indicated by the black arrowhead), which is characteristic for a phase transition from higher orthorhombic symmetry to lower monoclinic symmetry (Li et al., 2011; Ge et al., 2016a) for the ABMo$_3$O$_{12}$ family. Distinct changes of the Raman spectra occur for higher content of Zn$^{2+}$. The new Raman bands at about 175, 328, 772, 943, and 1008 cm$^{-1}$ correspond well to HfMo$_2$O$_8$ (Liang et al., 2008b) and that around 968 cm$^{-1}$ arises from ZnMoO$_4$ (Ahsaine et al., 2016). Both XRD and Raman analyses demonstrate that a single phase solid solution of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ is only possible for $x \leq 0.5$ and additional phases of HfMo$_2$O$_8$ and ZnMoO$_4$ form for $x \geq 0.6$. At RT, HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ for $x \leq 0.4$ adopt an orthorhombic structure while HfMg$_{0.5}$Zn$_{0.5}$Mo$_3$O$_{12}$ crystallizes in a monoclinic structure.

Raman spectroscopy is very sensitive to the monoclinic-to-orthorhombic phase transition (Li et al., 2011, 2016; Ge et al., 2016a). In order to get some insights into the influence of Zn$^{2+}$ on the phase transition, we carried out temperature-dependent
Raman spectral observation of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ ($x \leq 0.5$) as shown in Figure 2. The XRD analyses suggest that HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ ($x \leq 0.5$) have similar open framework structure as HfMgMo$_3$O$_{12}$. In the orthorhombic phase, there are four molecular formulas in a unit cell, in which each MoO$_4$ tetrahedron sharing its four vortexes with HfO$_6$/MgO$_6$ octahedra and each HfO$_6$/MgO$_6$ octahedron shares its corners with six MoO$_4$ tetrahedra. Hf and Mg are alternatively aligned in the [010] direction forming a quasi-layered structure (Omoté et al., 2011). The Raman modes from 1,050 to 900 cm$^{-1}$, from 900 to 750 cm$^{-1}$, from 400 to 320 cm$^{-1}$, and from 320 to 280 cm$^{-1}$ are identified as symmetric stretching ($v_1$), asymmetric stretching ($v_3$), asymmetric bending ($v_5$), and symmetric bending ($v_2$) modes in the MoO$_4$ tetrahedra, respectively (Liang et al., 2008a; Li et al., 2011). Figure 2A shows the temperature dependent Raman spectra of HfMgMo$_3$O$_{12}$. The most distinctive change of the Raman spectra is the disappearance of the band at about 1,001 cm$^{-1}$ with temperature increase from 168 to 178 K, which can be regarded as characteristic of the phase transition from low temperature monoclinic to high temperature orthorhombic structure (Li et al., 2011; Ge et al., 2016a). The phase transition temperature agrees well with the result derived from XRD analysis (Miller et al., 2012). In Figures 2B–F we present the temperature dependent Raman spectra for Zn$^{2+}$-containing samples. It is shown that the vanishing of the characteristic Raman band for the monoclinic structure occurs in the ranges of 168–178, 203–213, 223–233, 258–268, 283–293, and 318–328 K for $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5, respectively, demonstrating that the phase transition temperature increases with the content of Zn$^{2+}$.

In the orthorhombic structure of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ ($x \leq 0.5$), the four vortexes of each MoO$_4$ tetrahedron are shared with two HfO$_6$ and two MgO$_6$/ZnO$_6$ octahedra while each HfO$_6$/MgO$_6$/ZnO$_6$ octahedron shares its corners with six MoO$_4$ tetrahedra. Statistically, each MoO$_4$ tetrahedron links to 0.0, 0.2, 0.4, 0.8, and 1.0 ZnO$_6$ octahedron for $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5. Since the ionic radius of Zn$^{2+}$ is 74 pm which is slightly larger than that of Mg$^{2+}$ (72 pm), large lattice distortion and increase in phase transition temperature is not expected if only the ionic radius is considered. The experimentally observed obvious increase in phase transition temperature is therefore attributed to the difference in electronegativity between Zn$^{2+}$ (1.65 Pauling) and Mg$^{2+}$ (1.31 Pauling). Replacement of Mg$^{2+}$ by Zn$^{2+}$ causes an increase in electronegativity at the Zn$^{2+}$-cation side and a decrease in the effective negative charge on oxygen, and hence a decrease in the oxygen-oxygen repulsion. With increasing the content of Zn$^{2+}$, oxygen-oxygen attractive forces increase, causing the network collapse transition to occur at higher temperatures (Evans et al., 1997b).

Figure 3 shows the relative length changes of sintered cylinders with increasing temperature measured by dilatometry. All the samples for $x \leq 0.6$ exhibit abrupt length increase around the temperature of monoclinic to orthorhombic phase transition. The phase transition temperature increases with increasing the content of Zn$^{2+}$ except the one for $x = 0.6$ whose phase transition temperature is lower than that of $x \leq 0.5$ due to the generation of HfMo$_2$O$_8$ and ZnMoO$_4$. In this case, it can be deduced that the real content of Zn$^{2+}$ in HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ is lower than HfMg$_{0.5}$Zn$_{0.5}$Mo$_3$O$_{12}$. These results comply well with the above Raman spectroscopic analyses. The CTEs are calculated from the relative length change and shown in the Table 1. It indicates that all the single phase samples present excellent near-ZTE property above the phase transition temperature. It is interesting to notice that even for the multi-phase samples for $x = 0.8$ and 1.0, a near-ZTE property in a wide temperature range are realized. However, in this paper we focus on the effect of Zn$^{2+}$ incorporation on the structure and properties of the single phase HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$.

In order to get insight into the axial thermal expansion property, we carried out temperature-dependent powder XRD measurements for the samples of $x = 0.2$ and 0.3. For comparison, variable-temperature XRD data of HfMgMo$_3$O$_{12}$ were also collected. Figure 4A shows the selected temperature-dependent XRD patterns for HfMg$_{0.2}$Zn$_{0.8}$Mo$_3$O$_{12}$ at different temperatures. It is obvious that its XRD pattern changes distintively around 225 K, which is attributed to the phase transformation from lower temperature monoclinic to higher temperature orthorhombic structure. Lattice constants and cell volume at each temperature are calculated and given in Figure 4B. It is evident that the $a$- and $c$-axes contract while the $b$-axis expands with increasing temperature. The CTEs for the $a$-, $b$-, and $c$-axes and

![Figure 3](image-url)
volume are calculated to be $a_x = -2.70 \times 10^{-6} \, \text{K}^{-1}$, $a_y = 5.30 \times 10^{-6} \, \text{K}^{-1}$, $a_z = -1.72 \times 10^{-6} \, \text{K}^{-1}$, $a_l = 0.86 \times 10^{-6} \, \text{K}^{-1}(350 - 573 \, \text{K})$, respectively. This gives rise to a linear CTE $\alpha_l = 0.29 \times 10^{-6} \, \text{K}^{-1}$. Similar axial thermal expansion behaviors are obtained for HfMg$_2$Zn$_2$Mo$_3$O$_{12}$ from temperature dependent XRD measurements (not shown here). The changes of its lattice constants and volume with temperature are given in Figure 4C. The CTEs for the $a$, $b$, and $c$-axes and volume are calculated to be $a_x = -2.26 \times 10^{-6} \, \text{K}^{-1}$, $a_y = 5.21 \times 10^{-6} \, \text{K}^{-1}$, $a_z = -1.80 \times 10^{-6} \, \text{K}^{-1}$, $a_V = 1.12 \times 10^{-6} \, \text{K}^{-1}$, respectively, corresponding to a linear CTE $a_l = 0.37 \times 10^{-6} \, \text{K}^{-1}(350 - 573 \, \text{K})$. These results are consistent with the values measured by dilatometry, confirming HfMg$_{0.7}$Zn$_{0.3}$Mo$_3$O$_{12}$ and HfMg$_{0.8}$Zn$_{0.2}$Mo$_3$O$_{12}$ being intrinsically ZTE materials. Figure 4D shows the changes of lattice constants and volume of HfMgMo$_3$O$_{12}$ with temperature.

Considering the fact that the intrinsic linear CTE of HfMgMo$_3$O$_{12}$ is $1.02 \times 10^{-6} \, \text{K}^{-1}$ (Marinkovic et al., 2008), it is reasonable to conclude that the incorporation of Zn$^{2+}$ reduces the linear CTE and results in near ZTE of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$. A comparison of the axial CTEs for HfMgMo$_3$O$_{12}$, HfMg$_{0.8}$Zn$_{0.2}$Mo$_3$O$_{12}$, and HfMg$_{0.7}$Zn$_{0.3}$Mo$_3$O$_{12}$ are given in Table 2. It is found that partial substitution of Mg$^{2+}$ by Zn$^{2+}$ leads to a significant reduction of the CTE in the $b$-axis and an increase of the NTE in the $c$-axis, resulting in a near ZTE and lower anisotropy of thermal expansion in the Zn-containing compounds with respect to HfMgMo$_3$O$_{12}$ (see Table 2). The anisotropy of thermal expansion is defined as the maximum difference in the axial thermal expansion coefficients (Srikanth et al., 1992; Miller et al., 2013). The near zero linear thermal expansion and lower anisotropy property of the Zn-containing compounds suggest that they could withstand higher thermal shock resistance.

The difference in the linear CTEs measured by XRD and dilatometry could be understood by the microstructural effects. In contrast to XRD measurement which gives the thermal expansion property of cell lattice, dilatometry reveals the bulk thermal expansion property, including both intrinsic (thermal expansion of a material arising from the lattice dynamics) and extrinsic (thermal expansion related to microstructures such as texture, grain size, grain boundaries, poses, and microcracks) effects. The difference measured by the two methods reflects the extrinsic effect in the sintered bulk, which, on heating, can add a small negative component to the intrinsic linear expansion coefficients. Generally speaking, a smaller difference suggests a better sintered quality of the bulk material which is desired for most applications. The absolute differences for the Zn-containing compounds ($\Delta a_x = 0.42 \times 10^{-6} \, \text{K}^{-1}$ for $x = 0.2$ and $\Delta a_y = 0.38 \times 10^{-6} \, \text{K}^{-1}$ for $x = 0.3$) are obviously smaller than that for HfMgMo$_3$O$_{12}$ ($\Delta a_l = 1.17 \times 10^{-6} \, \text{K}^{-1}$). It means that partial substitution of Mg$^{2+}$ by Zn$^{2+}$ in HfMgMo$_3$O$_{12}$ could...
TABLE 2 | Intrinsic thermal expansion coefficients (\(\alpha\)) for HfMg\(_{1-x}\)Zn\(_x\)Mo\(_3\)O\(_{12}\) and HfMg\(_{0.8}\)Zn\(_{0.2}\)Mo\(_3\)O\(_{12}\) as obtained from variable-temperature XRD and literature and experimental values for HfMgMo\(_3\)O\(_{12}\).

| Sample (Structure) | Fit range (K) | \(\alpha_a\) (10\(^{-6}\) K\(^{-1}\)) | \(\alpha_b\) (10\(^{-6}\) K\(^{-1}\)) | \(\alpha_c\) (10\(^{-6}\) K\(^{-1}\)) | \(\alpha_l\) (10\(^{-6}\) K\(^{-1}\)) | \(\Delta\alpha_{\text{max}}\) (10\(^{-6}\) K\(^{-1}\)) | References |
|--------------------|---------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----------|
| HfMgMo\(_3\)O\(_{12}\) (Orthorhombic) | 298–1,013 | –3.44 | 8.0 | –1.49 | 1.02 | 11.44 | Marinkovic et al., 2008 |
| HfMgMo\(_3\)O\(_{12}\) (Orthorhombic) | 253–573 | –2.26 | 6.61 | –1.48 | 0.96 | 8.87 | This work |
| HfMg\(_{0.8}\)Zn\(_{0.2}\)Mo\(_3\)O\(_{12}\) (Orthorhombic) | 350–573 | –2.26 | 5.21 | –1.80 | 0.37 | 7.47 | This work |
| HfMg\(_{0.7}\)Zn\(_{0.3}\)Mo\(_3\)O\(_{12}\) (Orthorhombic) | 350–573 | –2.70 | 5.30 | –1.72 | 0.29 | 8 | This work |

**FIGURE 5** | SEM images of HfMg\(_{1-x}\)Zn\(_x\)Mo\(_3\)O\(_{12}\) with \(x = 0.0\) (A1), 0.1 (B1), 0.2 (C1), 0.3 (D1), 0.4 (E1), and 0.5 (F1).

**FIGURE 6A** | Schematic diagram of HfMgMo\(_3\)O\(_{12}\) to help us understand the mechanism of the phenomenon. In HfMg\(_{1-x}\)Zn\(_x\)Mo\(_3\)O\(_{12}\) (\(x \leq 0.5\)), Zn\(^{2+}\) is expected to substitute for Mg\(^{2+}\) due to the same valence and similar cation radius and each ZnO\(_6\) octahedron shares all its corners with six
MoO$_4$ tetrahedra. In order to see the bond strength changes induced by local electronic environment upon substitution of Zn$^{2+}$ for Mg$^{2+}$, we show in Figure 6B the Raman spectra of the stretching region for $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5. It is obvious that all the stretching modes shift successively to lower wavenumbers with increasing the content of Zn$^{2+}$, indicating a softening of the Mo-O bonds upon incorporation of Zn$^{2+}$. Once an Mg$^{2+}$ is replaced by Zn$^{2+}$, the local electronic equilibrium around the MoO$_4$ tetrahedron is broken. Zn$^{2+}$ has obviously a higher electronegativity and ability to drag electrons to the ZnO$_6$ octahedron from its connected six MoO$_4$ tetrahedra than Mg$^{2+}$, resulting in the weakening of the Mo–O bonds. The differences in ionic radius and electronegativity could cause a slight rotation of the connected polyhedra and hence the M-O-M linkages. This is probably the reason that the positive expansion of the $b$-axis is pronouncedly reduced and the NTE in the $c$-axes becomes more negative, resulting hence in a lower anisotropy in thermal expansion and near-zero CTEs of the Zn-containing compounds. Due to the large difference in electronegativity between Zn$^{2+}$ (1.65 Pauling) and Mg$^{2+}$ (1.31 Pauling), the more of Zn$^{2+}$ is incorporated, the more of the MoO$_4$ tetrahedra get distorted as revealed by Raman spectroscopy, resulting in larger distortion and instability of the lattice. When the forming energy for the single phase exceeds that for the multi-phases, then the multi-phases form.

Figure 6C shows the temperature-dependent Raman spectra of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ in the low wavenumber region. Obvious change of the Raman spectra occur between 203 and 213 K, corresponding to the monoclinic to orthorhombic phase transition, such as the appearance of new Raman modes at about 27, 44, 86, 159, and 182 cm$^{-1}$. The modes at about 44 and 86 cm$^{-1}$ are split into two or three modes in the low temperature phase and become degenerated in the high temperature phase. The low wavenumber modes arise from the external librational and translational vibrations of the connected octahedra–tetrahedra, or the librational and translational motions of metal ions in the Hf(Mg/Zn)–O–Mo linkages, which can also be regarded as the transverse vibrations of the bridging oxygen from the point of view of relative movement. Such an harmonic vibrations along with the distortion of the polyhedra are believed to be the origin of the NTE in the open framework structure since they bring the two end atoms closer upon heating (Evans, 1999; Ding et al., 2008; Marinkovic et al., 2009; Wang et al., 2013).

**CONCLUSION**

Solid solutions of HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ with near-ZTE are successfully synthesized by solid state reaction and the effects of Zn$^{2+}$ incorporation on the phase formation, thermal expansion, phase transition, and vibrational properties and micro-morphologies are investigated by XRD, dilatometry, Raman spectroscopy, and SEM. It is shown that (i) single phase formation is only possible for $x \leq 0.5$, otherwise, additional phases of HfMg$_2$O$_3$ and ZnMoO$_4$ generate; (ii) HfMg$_{1-x}$Zn$_x$Mo$_3$O$_{12}$ crystallize in an orthorhombic structure for $x \leq 0.4$ and in a monoclinic structure for $x = 0.5$ at RT; (iii) The phase transition temperature from monoclinic to orthorhombic structure increases with the content of Zn$^{2+}$, which occurs within 168–178, 203–213, 223–233, 258–268, 283–293, and 318–328 K for $x = 0.0, 0.1, 0.2, 0.3, 0.4$, and 0.5, respectively; (iv) The incorporation of Zn$^{2+}$ leads to an
pronounced reduction in the positive expansion of the b-axis and an enhanced NTE in c-axes, making the Zn-containing materials exhibit near-ZTE over a wide temperature range and lower anisotropy in thermal expansion in the orthorhombic phase; (v) Replacement of Mg$^{2+}$ by Zn$^{2+}$ breaks the local electronic equilibrium around the MoO$_4$ tetrahedron and weakens the Mo–O bonds, leading to obvious red shifts of all the Mo–O stretching modes with increasing the content of Zn$^{2+}$ due to obviously higher electronegativity of Zn$^{2+}$ than Mg$^{2+}$; (vi) The incorporation of Zn$^{2+}$ improves sintering property of samples, minimizing the possible contributions of extrinsic effects such as pores, which is preferred for most applications.

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AUTHOR CONTRIBUTIONS

EL conceived the idea and supervised the research. SL and RS are in charge of the synthesis and part measurements of the materials. XG, HY, and DC are in charge of the thermal expansion and Raman characterization. JG and MC are in charge of the XRD characterization and structural analyses. SL, XG, and EL are in charge of the manuscript preparation.

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Conflict of Interest Statement: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. 

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