Phase transition and near-zero thermal expansion in $\text{ZrFeMo}_2\text{VO}_{12}$

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ABSTRACT

$\text{ZrFeMo}_2\text{VO}_{12}$ material was successfully synthesized by solid-state method. The structure, phase transformation and thermal expansion of such material were studied by X-Ray powder diffraction (XRD), Raman spectra and thermal dilatometry. It crystallizes in monoclinic structure at room temperature (RT). The monoclinic structure transforms to orthorhombic structure on temperature at between 298 and 312 K. The coefficient of thermal expansion (CTE) was measured by dilatometer to be $(0.36 \pm 0.02) \times 10^{-6} \text{ K}^{-1}$ (401~573 K) and calculated by XRD data to be $(0.68 \pm 0.17) \times 10^{-6} \text{ K}^{-1}$ (423~573 K). Both the values of intrinsic (XRD) and extrinsic (dilatometric) thermal expansion are near zero.

Keywords: Negative thermal expansion; Near-zero thermal expansion; Phase transition; Raman

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1. Introduction

Near-zero thermal expansion materials are particularly needed in the fields such as precision optics, optoelectronics and nanometer materials. It is because that most materials expand on heating that may induce thermal stresses and result in failure of devices. To solve this problem, extensive researches have been carried out on negative thermal expansion (NTE) materials, for which can be combined with positive thermal expansion materials or tailored chemically to attain near zero thermal expansion materials. Series of NTE materials have been found such as AM_2O_7 ($A = \text{Zr, Hf}$; $M = \text{V, P}$) [1-3], AM_2O_8 ($A = \text{Zr, Hf}$; $M = \text{W, Mo}$) [4-8] and $A_2M_3O_{12}$ ($A = \text{transition metal or rare earth}$; $M = \text{W, Mo}$) [9, 10]. Among the materials with flexible framework structure, $A_2M_3O_{12}$ family materials can exhibit stable NTE over a wide temperature range. Furthermore, the thermal expansion coefficient (TEC) of $A_2M_3O_{12}$ can be adjusted by varying the type and content of the substitution of cation, which provides a possible way to prepare materials with adjustable TEC, especially those with zero TEC [11]. Related reports include $(Al_{2x}(HfMg)_{1-x})(WO_4)_3$ [12], $In(HfMg)_{0.5}Mo_3O_{12}$ [13], $Sc_{2-x}Fe_xMo_3O_{12}$ [14], $Fe_{2-x}Y_xMo_3O_{12}$ [15], $Fe_{2-x}(ZrMg)_{0.5x}Mo_3O_{12}$ [16], etc.

Many members of $A_2M_3O_{12}$ family undergo a phase transition from monoclinic to orthorhombic phase upon heating. The phase transition temperatures for $Al_2W_3O_{12}$, $Al_2Mo_3O_{12}$, $Cr_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, $In_2Mo_3O_{12}$, $Sc_2(MoO_4)_3$ have been observed and reported by Sleight and Bixner [17] to be 267K, 473K, 658K, 772K, 628K and 282K, respectively. For near-zero thermal expansion materials associated with them, the phase transition temperature of $In(HfMg)_{0.5}Mo_3O_{12}$, $Sc_{2-x}Fe_xMo_3O_{12}$ ($x = 0.7$), $Fe_{2-x}Y_xMo_3O_{12}$ ($x = 0.5$), $Fe_{2-x}(ZrMg)_{0.5x}Mo_3O_{12}$ ($x = 1.7$) were reported to be 425 K, 385 K, below 103 K, below 103 K, respectively [13-16]. Normally orthorhombic structure with corner-sharing AO_6 octahedra and MO_4 tetrahedra can

accommodate for transverse thermal vibrations which are responsible for NTE [18]. The magnitude of the NTE in $A_2M_3O_{12}$ family is related to the size of cation according to Forster et al. [19] Apart from A^{3+} cationic size, there may exist other factors that can influence the thermal expansion properties of some systems. It is suggested that the strength of $A^{3+} - O$ bond in $A_2M_3O_{12}$ also plays a role in NTE behavior of the materials [20]. Additionally, Sleight et al. [17] investigated the relation between the phase transition temperature and A^{3+} cation in $A_2M_3O_{12}$ and found that the phase transition temperature doesn't depend on the size of A^{3+} cation but increases with the electronegativity (EN) of A^{3+} cation increasing. In practice, high phase transition temperature hinders the extensive application of the materials. Thus lowering the phase transition temperature to far below RT combined with tailoring the CTE is particularly important.

In order to lower the transition temperature of $Fe_2Mo_3O_{12}$, some researches considered partial substitution of Fe^{3+} by other cations. Our previous study on substitution of Y^{3+} for Fe^{3+} found that the phase transition temperature can be effectively reduced (minimum below 103 K) with increasing the contents of Y^{3+} in $Fe_{2-x}Y_xMo_3O_{12}$ series materials [15]. However, these materials are highly hygroscopic due to large cation radius of Y^{3+} and show NTE after complete release of crystal water. By substitutional co-incorporation of Zr^{4+} and Mg^{2+} , the phase transition temperatures of $Fe_{2-x}(ZrMg)_{0.5x}Mo_3O_{12}$ ($x = 0-1.8$) compounds were found to be lowered significantly (minimum below 103K) [16]. The phase transition temperature of $Sc_{2-x}Fe_xMo_3O_{12}$ materials decreased (minimum 385K) with reducing Fe content according to Wu et al. [14]. The phase transition temperatures of the solid solutions $Cr_{2x}Fe_{2-2x}Mo_3O_{12}$ and $Al_{2x}Fe_{2-2x}Mo_3O_{12}$ ($0 < x < 1$) have been reported to be between those of their two constitutional compounds ($A_2Mo_3O_{12}$) [20], that is, still far above RT. Dual-substitution for Fe^{3+} and Mo^{6+} has not yet been reported. What will happen when both Fe^{3+} and Mo^{6+} cations are substituted by Zr^{4+} and V^{5+}

cations in $\text{Fe}_2\text{Mo}_3\text{O}_{12}$? In present work, we studied the effects of double-cations substitution in $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ material on the phase transition temperature and the CTE.

In this paper, we report a near-zero thermal expansion material of $\text{ZrFeMo}_2\text{VO}_{12}$. Using XRD, Raman spectra and thermal dilatometry we investigated the structure, phase transition and NTE of the material. Results showed that the prepared material adopts monoclinic structure with space group P2/m (10) at RT. Structure phase transition from monoclinic to orthorhombic phase (space group Pbcn (60)) occurs at 298~312 K, much lower than that of $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (772 K). The CTE was measured by XRD to be $\alpha_t = (0.68 \pm 0.17) \times 10^{-6} \text{ K}^{-1}$ and measured by dilatometer to be $\alpha_t = (0.36 \pm 0.02) \times 10^{-6} \text{ K}^{-1}$ in the similar range of temperature (about 401~573 K). Both the values of CTE are much near zero, and obviously different from the parent material $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ ($-14.82 \times 10^{-6} \text{ K}^{-1}$) [21]. The tiny difference between XRD and dilatometry might be caused by the effects of microstructure [22].

2. Experimental Details

$\text{ZrFeMo}_2\text{VO}_{12}$ sample was synthesized by standard solid-state reaction method. Stoichiometric quantities of commercial chemicals of ZrO_2 (99%), Fe_2O_3 (99%), V_2O_5 (99%) and MoO_3 (99.5%) were ground together thoroughly with an agate mortar for 2 h. The mixed powder was heated from RT to 973 K in a furnace at a rate of 5 K/min, maintained at 973 K for 4 h, and cooled down slowly in the furnace. The sintered powder was reground, pressed into pellets with length about 3.5 mm and diameter 13 mm then sintered again at 973K for 2 h. The obtained compact pellets were kept for measurements of linear CTEs.

AXIS SUPRA (Kratos) X-ray photoelectron spectroscopy (XPS) was used to analyze the composition of the synthesized sample. Variable-temperature XRD was performed on a D8 ADVANCE X-ray diffractometer (Germany Bruker) with $\text{Cu K}\alpha_1$ radiation. Diffraction data

were collected with a step size of 0.01° in the 2θ range of $10\text{--}80^\circ$. Using FullProf software, unit cell dimensions below and above the phase transition temperature were determined with LeBail fit and Rietveld methods, respectively. Orthorhombic $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (ICSD code 080449) was used as the starting refined model. A LabRAM HR Evolution Raman spectrometer (France HORIBA Jobin Yvon S.A.A.) with 532/633 nm laser wavelength excitation was used for variable-temperature/RT Raman spectroscopic studies. The linear CTE was measured with a dilatometer (LINSEIS DIL L75/L76) at the heating and cooling rates of 5K/min.

3. Results

3.1 Crystal structure at RT

Fig. 1 (a) shows the XPS survey spectrum of $\text{ZrFeMo}_2\text{VO}_{12}$ at RT. Semi-quantitative XPS analyses reveals that the atomic ratio of the element Zr, Fe, Mo, V and O of the prepared sample is about 5.94 : 5.75 : 12.06 : 5.28 : 70.97, which is close to the theoretical calculation result (5.88 : 5.88 : 11.76 : 5.88 : 70.59). The element C comes from the oil pump. The Fe 2p XPS spectra of $\text{ZrFeMo}_2\text{VO}_{12}$ were observed at 710.25 and 724.65 eV for $2p_{3/2}$ and $2p_{1/2}$ peaks, respectively, as shown in Fig. 1 (b). The binding energies of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ confirms that the Fe ions in $\text{ZrFeMo}_2\text{VO}_{12}$ are in +3 valance state. From Fig. 1 (c), the binding energies of V $2p_{3/2}$ and V $2p_{1/2}$ for the sample are 516.30 and 523.80 eV, respectively, suggesting that V ions are in +5 valance state.

Fig. 1 (d) shows the LeBail fit of the 297 K XRD pattern of $\text{ZrFeMo}_2\text{VO}_{12}$ using the P2/m (10) space group. The least-squares refinement resulted in χ^2 (goodness-of-fit) values ($\chi^2 = \text{Rwp/Rexp}$) about 2.02. The cell parameters were calculated as follows: $a = 13.5208 \text{ \AA}$, $b = 12.9329 \text{ \AA}$, $c = 12.5732 \text{ \AA}$, $\alpha = 90.000^\circ$, $\beta = 110.927^\circ$, $\gamma = 90.000^\circ$, $V = 2053.5654 \text{ \AA}^3$. It is indicated that $\text{ZrFeMo}_2\text{VO}_{12}$ adopts monoclinic structure with space group P2/m (10) at RT.

Besides, no peaks other than those of monoclinic structure were present in the XRD pattern, which ruled out the possibilities of impurity phases within the detection limit of XRD.

Fig. 1 (a) XPS survey spectrum of $\text{ZrFeMo}_2\text{VO}_{12}$ at RT. (b) The XPS spectrum of Fe 2p for the sample. (c) The XPS spectrum of V 2p for the sample. (d) LeBail fit of the 298 K XRD pattern of $\text{ZrFeMo}_2\text{VO}_{12}$ using the P2/m (10) space group.

3.2 Phase transition

Fig. 2a shows the XRD patterns of $\text{ZrFeMo}_2\text{VO}_{12}$ at different temperatures. It can be seen that the apparent difference of the pattern at 297 K (RT) from the others is the appearance of the peak at 27.0° (Miller index (113)). It indicates that the RT structure is changed with temperature increasing. Besides, there are no obvious peaks to appear/disappear for the XRD patterns from

312 to 573 K, suggesting that a non-monoclinic structure maintains with temperature increasing. The non-monoclinic structure is found consistent well with orthorhombic $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (space group pbcn (60)). It is obvious that a phase transition from monoclinic to orthorhombic phase occurs at RT~ 312 K.

Fig. 2 (a) XRD patterns of $\text{ZrFeMo}_2\text{VO}_{12}$ measured at different temperatures. Peaks are indexed for the patterns of 297 K and 573 K. (b) Results of the Rietveld analysis of the XRD pattern for $\text{ZrFeMo}_2\text{VO}_{12}$ at 312 K ($R_p = 20.4\%$, $R_{wp} = 19.5\%$, and $R_{exp} = 11.25\%$).

The Rietveld refinement of XRD pattern at 312 K are given in Fig. 2b. The Rietveld reliability factors are as follows: $R_p = 20.4\%$, $R_{wp} = 19.5\%$, $R_{exp} = 11.25\%$, $\chi^2 = R_{wp}/R_{exp} = 1.73$. The calculated values of cell parameters are: $a = 12.9406 \text{ \AA}$, $b = 9.3402 \text{ \AA}$, $c = 9.4336 \text{ \AA}$, $V =$

1140.2172 Å³. The refined results further indicated that ZrFeMo₂VO₁₂ adopts orthorhombic structure with space group Pbcn (60) when temperature is at or above 312 K.

Fig. 3 (a) Raman spectra of ZrFeMo₂VO₁₂ at different temperatures. (b) and (c) are the partial amplification of (a). (d) multi-peak fits of the Raman bands in 900~1050 cm⁻¹ (The black lines indicate the measured intensities and the red lines represent the fitted Raman curve).

Apart from XRD, variable-temperature Raman spectra were also used to analyze the phase transition. Fig. 3a shows the temperature dependence of the Raman spectra of ZrFeMo₂VO₁₂. Based on the frequencies of MoO₄ ions in other molybdates [23] one can assign the internal modes in this material. The Raman modes in the ranges 900–1050, 750–950 and 300–400 cm⁻¹ can be identified as the internal symmetric stretching ν_1 , asymmetric stretching ν_3 and bending

vibrations (ν_2 and ν_4) of the MoO_4 or VO_4 tetrahedra and those below 300 cm^{-1} are translational and librational motions of the FeO_6 or ZrO_6 polyhedra. As shown by Fig. 3b and Fig. 3c, there are obvious changes in the Raman spectra around 783 cm^{-1} and 980 cm^{-1} . Raman bands around 778 cm^{-1} and 975 cm^{-1} successively shift to the higher wavenumber and finally disappear with temperature increasing from 134 to 298 K. However new Raman bands around 783 cm^{-1} and 980 cm^{-1} appear at 314 K and successively shift to the lower wavenumber with temperature increasing. Fig. 3d illustrates the changes of Raman bands by multi-peak fit. The Raman band at about 1000 cm^{-1} is characteristic for monoclinic structure [15, 16, 23-25] which can be seen for the spectra from 134 K to 298 K but disappears at 314 K. It is obvious that there is a phase transition at $298 \sim 314\text{ K}$, which agrees well with the result of variable-temperature XRD.

3.3 Thermal expansion property

Fig. 4A shows dependence of the lattice constants on temperature of orthorhombic $\text{ZrFeMo}_2\text{VO}_{12}$ from 312 to 573 K. It can be seen that a-axis expands while b-axis and c-axis contract linearly with temperature increasing. The CTEs from 423 to 573 K are calculated to be $7.93 \times 10^{-6}\text{ K}^{-1}$, $-2.27 \times 10^{-6}\text{ K}^{-1}$, $-3.62 \times 10^{-6}\text{ K}^{-1}$ for a, b and c axes, respectively. This gives rise to a volume CTE of $2.04 \times 10^{-6}\text{ K}^{-1}$ and a linear CTE of $0.68 \times 10^{-6}\text{ K}^{-1}$ with an uncertainty of $\pm 0.17 \times 10^{-6}\text{ K}^{-1}$. It can be concluded that orthorhombic $\text{ZrFeMo}_2\text{VO}_{12}$ exhibits anisotropic thermal expansion properties and near-zero linear CTE.

Fig. 4B shows relative length change of $\text{ZrFeMo}_2\text{VO}_{12}$ measured by dilatometry. Due to the apparent phenomenon of thermal hysteresis in the curve, only the heating section is given. An expansion with CTE of $(17.80 \pm 0.35) \times 10^{-6}\text{ K}^{-1}$ (RT $\sim$ 350 K) and $(5.22 \pm 0.12) \times 10^{-6}\text{ K}^{-1}$ (351 $\sim$ 400 K) was observed, followed by a near-zero thermal expansion in the temperature region of 401 to 673 K. The appearance of tuning in the thermal expansion curve can be

explained as monoclinic to orthorhombic structure phase transition accompanied by a large volume change. The phase transition has been demonstrated by variable-temperature XRD and variable-temperature Raman spectra. The linear CTE from 401 to 573 K is calculated to be about $(0.36 \pm 0.02) \times 10^{-6} \text{ K}^{-1}$, slightly different from the XRD measurements. The microstructural effects might be the cause of such difference. The CTE calculated from XRD reveals the intrinsic thermal expansion of unit cell while that measured from dilatometry reflects the thermal expansion of bulk material, in which microcracks and pores are inevitable and may affect the measured result. Also the difference between intrinsic (XRD) and extrinsic (dilatometric) thermal expansion can be found in $\text{Al}_2\text{W}_3\text{O}_{12}$ [9, 26], $\text{In}(\text{HfMg})_{0.5}\text{Mo}_3\text{O}_{12}$ [13], etc.

Fig. 4 (A) Temperature dependence of orthorhombic unit cell parameters: obtained from Rietveld refinement of XRD data. (B) Relative length change of $\text{ZrFeMo}_2\text{VO}_{12}$: obtained from dilatometric measurement. The inset diagram shows relative length change of samples with different Mo:V molar ratios.

3.4 Mechanism of phase transition and near-zero thermal expansion

The effect of substitution of $\text{Zr}^{4+}/\text{V}^{5+}$ for $\text{Fe}^{3+}/\text{Mo}^{6+}$ on the phase transition temperature is correlated with the electronegativity of cation [17]. Since the electronegativity of Zr^{4+} (1.33) is smaller than that of Fe^{3+} (1.83), and the electronegativity of V^{5+} (1.53) is smaller than that of Mo^{6+} (2.16), more negative charges are concentrated on the oxide ions, which results in more

repulsion between the oxide ions for $\text{ZrFeMo}_2\text{VO}_{12}$ than for the unsubstituted material. It has been reported that there is an abrupt decrease in volume when the structure transforms from orthorhombic to monoclinic phase (a volume collapse phase transition) [9]. More repulsion means more resistance to a volume collapse during the cooling process, which causes the phase transition to occur at a lower temperature for $\text{ZrFeMo}_2\text{VO}_{12}$ than for the unsubstituted material. While in the heating process, more repulsion implies more impetus to restore the volume from collapse, resulting in a lower phase transition temperature. It can be seen from the inset diagram of Fig. 4B that the phase transition temperature decreases with Mo:V molar ratio decreasing, which accords quite well with the theoretical results.

The NTE of orthorhombic $\text{A}_2\text{M}_3\text{O}_{12}$ was convincingly attributed to the bending of A–O–M linkages on increasing the temperature. And the bending of A–O–M linkages may be caused by the transverse vibrations of the bridging oxygen [27]. As can be seen in Fig. 5a, the orthorhombic $\text{ZrFeMo}_2\text{VO}_{12}$ also has A–O–M linkages (A = Zr/Fe, M = Mo/V). Considering the double-substitution of $\text{Zr}^{4+}/\text{V}^{5+}$ for $\text{Fe}^{3+}/\text{Mo}^{6+}$, the electronegativity of A^{3+} cation and the M–O bond strength can be used to analyze the NTE of $\text{ZrFeMo}_2\text{VO}_{12}$. Since the electronegativity of Zr^{4+} (1.33) is smaller than that of Fe^{3+} (1.83), the effective negative charge of oxygen anions increases, resulting in larger oxygen–oxygen repulsion and hence more rigid polyhedra. As shown in Fig. 5b, the stretching Raman band around 980 cm^{-1} shift to the higher wavenumber with Mo:V ratio decreasing, which suggests that M–O bond becomes stronger or harder with the content of V increasing. As a result, it is expected that the extent of bending, as mentioned by Tyagi [21], will be less in Zr–O–V (Mo) linkages or Zr (Fe)–O–V linkages than in Fe–O–Mo linkages. Consequently, the substitutions of Zr^{4+} and V^{5+} result in near-zero thermal expansion.

Fig. 5 (a) Rietveld-refined structure of $\text{ZrFeMo}_2\text{VO}_{12}$ at 312 K. O atoms are shown in red balls, $\text{Fe}(\text{Zr})\text{O}_6$ octahedron in green, and $\text{Mo}(\text{V})\text{O}_4$ tetrahedron shown in red. (b) RT Raman spectra of samples with different Mo:V molar ratios.

4. Conclusion

Using solid method, a new compound of $\text{ZrFeMo}_2\text{VO}_{12}$ was synthesized by double-substituting of $\text{Zr}^{4+}/\text{V}^{5+}$ for $\text{Fe}^{3+}/\text{Mo}^{6+}$. Structure phase transition from monoclinic to orthorhombic phase occurs at RT $\sim$ 312 K, which is much lower than that of $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ (772 K). The key factor influencing the phase transition temperature is the electronegativity of cation. Because of the smaller electronegativity of $\text{Zr}^{4+}/\text{V}^{5+}$ than that of $\text{Fe}^{3+}/\text{Mo}^{6+}$, there are more negative charge around the oxide ions in $\text{ZrFeMo}_2\text{VO}_{12}$ than in $\text{Fe}_2\text{Mo}_3\text{O}_{12}$, thus the repulsion force between the oxide ions is stronger in $\text{ZrFeMo}_2\text{VO}_{12}$ than in $\text{Fe}_2\text{Mo}_3\text{O}_{12}$ to resist to a

volume collapse, resulting in a low phase transition temperature in $\text{ZrFeMo}_2\text{VO}_{12}$. The CTE for $\text{ZrFeMo}_2\text{VO}_{12}$ was measured to be $(0.36 \pm 0.02) \times 10^{-6} \text{ K}^{-1}$ in the temperature range of 401 ~573 K by dilatometry while it was calculated to be $(0.68 \pm 0.17) \times 10^{-6} \text{ K}^{-1}$ (423 ~ 573 K) by XRD. The slightly difference between the two methods was attributed to the effects of microstructure. The thermal expansion properties of crystallographic axes a, b and c are anisotropic. The near-zero thermal expansion was explained as the less extent of bending of Zr–O–V (Mo) linkages or Zr (Fe)–O–V linkages than Fe–O–Mo linkages due to the harder Zr–O bond and V–O bond.

Acknowledgements

This work was supported by the National Science Foundation of China (Nos. 10974183, 11574276), Basic and Frontier Technology Research Program of Henan Province (142300410365), the fund for Science & Technology Innovation Team of Zhengzhou (2011-03), the Key Scientific Research Project of Colleges and Universities of Henan Province (15B140004).

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