Low thermal expansion over a wide temperature range of

$\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ ($0 \leq x \leq 0.9$)

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Abstract: A novel $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ ($0 \leq x \leq 0.9$) material is developed and the effect substitutions of $\text{Fe}^{3+}/\text{Mo}^{6+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$ in ZrV_2O_7 on the thermal expansion property are investigated. For the smaller x value ($x \leq 0.5$), **their crystal structures remain cubic. The one of $x=0.5$ is much higher than recent reports about uni-substitution of P^{5+} for V^{5+} and dual-substitution of $\text{Cu}^{2+}/\text{P}^{5+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$. For a substitution more than 0.5, crystal lattice appears distorted and $3 \times 3 \times 3$ superstructure disappears gradually.** For the substitution of $x=0.9$, low thermal expansion is obtained from 140 to 700 K, which holds great potential applications in low temperature field. The mechanism of low thermal expansion of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ ($0 \leq x \leq 0.9$) is discussed around the distortion of crystal structure due to the substitutions of $\text{Fe}^{3+}/\text{Mo}^{6+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$ in ZrV_2O_7 .

Keywords: Phase transitions; Thermal expansion; Crystal structure; Raman spectroscopy and scattering

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1. Introduction

Large difference in thermal expansion coefficients of materials can lead to thermal stress and even to failure when temperature changes abruptly. Negative thermal expansion (NTE) materials have attracted tremendous attention due to their potential applications in manufacturing zero thermal expansion devices and matching the coefficients of thermal expansion (CTE) between different materials [1-3]. However, some disadvantages of NTE materials limit their wide utilization, such as metastable structure [4,5], phase transition, hygroscopicity [6], anisotropy [7], etc. Plenty of investigations are focused on improving their properties, developing novel NTE materials. Both ZrW_2O_8 and ZrV_2O_7 exhibit isotropic NTE but ZrW_2O_8 is thermodynamically metastable at room temperature (RT). ZrV_2O_7 is one of the most attractive NTE materials because of its stable structure and isotropic property [8-10]. Nevertheless, ZrV_2O_7 belongs to a $3\times 3\times 3$ superstructure at room temperature (RT) and exhibits giant thermal expansion till 375 K above which it displays an isotropic NTE behavior up to 1073 K. There are two phase transitions at 350 and 375 K in ZrV_2O_7 [8-11]. The high temperature phase has the ideal parent structure, a framework structure with space group symmetry $P\bar{a}3$, $Z=4$. An X-ray diffraction (XRD) study has shown interesting high pressure behavior for ZrV_2O_7 , which undergoes a reversible phase transition at 1.38-1.72 GPa from α -phase (cubic) to β -phase (pseudo-tetragonal) [12,13].

Many efforts have been devoted to reduce the phase transition temperature of ZrV_2O_7 . Sleight et al. utilized P^{5+} to substitute V^{5+} for decreasing the phase transition temperature of $\text{ZrV}_{2-x}\text{P}_x\text{O}_7$ ($0\leq x\leq 2$) from 375 K ($x=0$) to 326 K ($x=0.3$) [14]. We recently found that the phase transition temperature of $\text{ZrV}_{2-x}\text{P}_x\text{O}_7$ ($0\leq x\leq 1$) decreased to 273 K ($x=0.8$) and 213 K

($x=1$) through temperature dependent Raman spectra but the CTE alters from low positive to negative at about 340 K when $x=0.4$ [15]. This was attributed to the incorporation of P in ZrV_2O_7 which liberates more free space in the lattice, making the bond angle of V-O-V extended and phase transition temperature decreased [14,15]. Aliovalent substitution of Mo^{6+} for V^{5+} [16] or W^{6+} for V^{5+} [17] in ZrV_2O_7 was also reported but the phase transition temperature could not be reduced obviously. Solid solutions of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ have been established [18], whose phase transition temperatures did not decrease either. Yanase et al. [19] showed that using (Nb^{5+} , Y^{3+}) to substitute Zr^{4+} in ZrV_2O_7 was more effective than using P substitution for V for the suppression of superstructure formation. Single ion substitution for Zr or V in ZrV_2O_7 mentioned above could induce distortion of crystal lattice due to difference in valence or radius and only a low substitution ratio could be realized. Dual-ion substitutions of $\text{Cu}^{2+}/\text{P}^{5+}$ or $\text{Fe}^{3+}/\text{P}^{5+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$ have been reported. However, it is difficult to reach a high solubility of the dopants [20,21]. Although it seems effective for suppression of the giant CTE in the low temperature range by substitution of P^{5+} for V^{5+} , or (Nb^{5+} , Y^{3+}) for Zr^{4+} , or $\text{Cu}^{2+}/\text{P}^{5+}$ or $\text{Fe}^{3+}/\text{P}^{5+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$, the turning point for CTE from positive to negative by dilatometry appears around 350 K. **However, strong efforts are also being done in the designing of zero CTE composite materials by combining negative CTE matrices with positive CTE second phases [22,23].**

In order to further reduce the phase transition temperature of ZrV_2O_7 , partial substitution for both Zr and V sites and enhancing the solubility of dopants may be necessary. In the present paper, we developed a $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ material using $\text{Fe}^{3+}/\text{Mo}^{6+}$ to substitute $\text{Zr}^{4+}/\text{V}^{5+}$ in ZrV_2O_7 , and investigated the substitution effect on their

thermal expansion properties in detail. It is shown that the solubility of $\text{Fe}^{3+}/\text{Mo}^{6+}$ is much higher than $\text{Cu}^{2+}/\text{P}^{5+}$ or $\text{Fe}^{3+}/\text{P}^{5+}$ in ZrV_2O_7 and the superstructure disappears for $x \geq 0.5$. A near zero thermal expansion from 190 to 700 K is obtained when $x = 0.8 \sim 0.9$.

2. Experimental

$\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ ($0.0 \leq x \leq 1.0$) were synthesized by a solid state method from Fe_2O_3 (99.0%, Tianjin Zhiyuan Chemical Reagent Co. Ltd.), ZrO_2 (99.0%, Tianjin Guangfu fine Chemical Research Institute), MoO_3 (99.5%, Tianjin Kaitong Chemical Reagent Co. Ltd.) and V_2O_5 (99.0%, Tianjin Kaitong Chemical Reagent Co. Ltd.). The raw materials were mixed according to stoichiometric amounts of Fe_2O_3 , ZrO_2 , MoO_3 and 7% excess V_2O_5 of desirable materials and ground in a mortar for 3 h, and then pressed into tablets with length about 10 mm and diameter 10 mm followed by sintering at 1023 K for 4 h.

XRD measurements were carried out with an X`Pert PRO X-ray Diffractometer. Temperature dependence of XRD was recorded by using a heating/freezing stage with an accuracy of ± 0.1 K. Raman spectroscopy (Renishaw MR-2000 Raman spectrometer) with a TMS 94 heating/freezing stage with an accuracy of ± 0.1 K was used to characterize the vibrational property of lattice. The linear thermal expansion coefficients were measured on dilatometers (LINSEIS DIL L75/L76), with the heating and cooling rates of 5 K/min.

3. Results and discussion

3.1 Crystal structure analysis

Fig. 1 shows the XRD patterns of as-prepared $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$. When $x = 0.0$, the primary diffraction peaks are corresponding to ZrV_2O_7 (JCPDF card: 88-0587) except for weak peaks indicating as “ ∇ ” for secondary phase ZrO_2 , which could relate to the

volatilization of V during the sintering process. However, comparing those diffraction peaks of the samples with $x=0.1$ and 0.3 , it can be observed that the secondary phase of ZrO_2 reduces obviously and even disappears for $x=0.3$. The result suggests that the substitutions of Fe/Mo for Zr/V suppress the formation of the secondary phase of ZrO_2 and the others, which could relate the easy combination of V with Fe and then low volatilization. The similar phenomenon was observed in Fe^{3+} -doped $\text{ZrV}_{1.6}\text{P}_{0.4}\text{O}_7$ [21]. From $x=0.3$ to $x=0.5$, the relative intensity of main diffraction peak at about 20° weakens to become secondary main peak but the primary peaks still remain that of $x=0$, indicating that the primary structure is the same crystal structure as that of ZrV_2O_7 . Nevertheless, besides the peaks shifting to higher angles, the former main peak at about 20° continues to weaken even to disappear and the former secondary peaks at about 23° and 25° split gradually, and even some new diffraction peaks emerge with further increasing substitution amounts of Fe^{3+} and Mo^{6+} from $x=0.6$ to $x=0.9$. The peaks splitting and new peaks show that the symmetry of crystal lattice lowers from cubic to orthorhombic or monoclinic with further increasing the substitutions of $\text{Fe}^{3+}/\text{Mo}^{6+}$ for $\text{Zr}^{4+}/\text{V}^{5+}$.

A slow RT XRD scan was collected for Rietveld analysis using the Fullprof software. The XRD data were refined in Pa-3 using cubic structure of ZrV_2O_7 as starting model. For $x=0.3$, mixed cation occupancies of Zr/Fe for all Zr sites and V/Mo for V sites are considered and excellent fits could be obtained [24]. Figs. 2a and 2c show the structure refinement results of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0.0$ and 0.3 . It is found that the cell parameter of a decreases from 8.77014 ($x=0.0$) to 8.73699 ($x=0.3$). In order to show directly the change of crystal structure when Fe/Mo substitute for Zr/V in ZrV_2O_7 , the

block buildings of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0.0$ and 0.3 are presented in Figs. 2b and 2d. The samples with $x=0.0$ and $x=0.3$ have similar cubic structures, while the octahedral in the building block with $x=0.3$ presents two different colors for 0.3Fe and 0.7Zr , and the tetragonal have the similar color of red due to much larger content of 1.7V than that of 0.3Mo . The substitution content reaches such large but the cubic structure still remains, which could relate to the interaction between the formed $(\text{Fe}_{\text{Zr}})^-$ and $(\text{Mo}_{\text{V}})^+$. As known, Fe^{3+} substituting Zr^{4+} results in one electron less than need for oxygen and one electron is more than need for oxygen when Mo^{6+} substituting V^{5+} , therefore, charged $(\text{Fe}_{\text{Zr}})^-$ and $(\text{Mo}_{\text{V}})^+$ are formed to respect electric neutrality as a whole crystal. In fact, there are competitions between Fe^{3+} and Zr^{4+} , Mo^{6+} and V^{5+} resulting in a probability for the crystal sites.

For higher substitutions of Fe/Mo for Zr/V in ZrV_2O_7 such as $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$, their crystal structures are different from that of ZrV_2O_7 as indicated by the distinct changes of the diffraction peaks. No suitable crystallographic information file is found, therefore, we calculated the crystal parameters of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ using the least-square method with PowderX program [25]. It is found that there are 87 lines out of the 88 experimental XRD peaks matching well with a monoclinic structure (see Fig. 3). The lattice parameters of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ are determined to be $a=8.48816\text{ \AA}$, $b=8.90565\text{ \AA}$ and $c=8.20447\text{ \AA}$ and $\alpha=90^\circ$, $\beta=112.736^\circ$, $\gamma=90^\circ$.

Fig. 4 shows the temperature dependent XRD patterns of $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Fe}_{0.9}\text{Zr}_{0.1}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ from RT to 873 K. With increasing temperature, the diffraction peaks

of $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ shift to smaller angles while those of $\text{Fe}_{0.9}\text{Zr}_{0.1}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ shift slightly to larger angles. These results suggest that $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ expands weakly whereas $\text{Fe}_{0.9}\text{Zr}_{0.1}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ contracts slightly with increasing temperature.

3.2 Low thermal expansion

Fig. 5A and 5B shows the temperature dependences of the lattice constants of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$, which were calculated from high-temperature XRD results (Fig. 4) using the least-square method with PowderX program. The linear and volumetric CTEs of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ on axis are shown in the Table 1. The lattice constants of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ increase with increasing temperature and that of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ decrease with increasing temperature. The temperature dependences of the cell volume of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ are shown in Fig. 5C. The cell volume of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ expands with increasing temperature and that of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ contracts with increasing temperature. The linear and volumetric CTEs of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ on axis are shown in the Table 1.

The linear relative length measurement is performed to calculate the coefficients of thermal expansion (CTEs) $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ (Fig. 5D), which are listed in Table 2. It can be clearly seen that the abrupt thermal expansion below 400 K according to $3\times 3\times 3$ superstructure was remarkably reduced for the samples with $x=0.0 \sim 0.5$, even though the phase transition temperature is not lowered. With further increasing the magnitude of substitution, no phase transition according to the abrupt thermal expansion is observed, indicating the disappearance of $3\times 3\times 3$ superstructure. This result is consistent with that of temperature dependent XRD. The linear CTEs measured by dilatometer are shown in Table 2.

The above results revealed that the anisotropic thermal expansion behavior obtained is

thus an intrinsic property of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$. Both the linear and other CETs of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ are lower than that of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ from RT to 700 K. The CETs discrepancy between XRD and dilatometer for $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ could relate to the formation of pores in the ceramics during the sintering process.

To further investigate the low thermal expansion property of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ ($x=0.9$), low temperature expansion measurement was also performed (Fig. 6). CET of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ was obtained to be $0.72 \times 10^{-6} \text{ K}^{-1}$ from 140 to 400 K. This result suggests that $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ has better low thermal expansion property at a relative low temperature range.

The low thermal expansion mechanism of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ can be mainly attributed to the distortion of crystal structure due to more substitutions of Fe/Mo for Zr/V in ZrV_2O_7 . Fe and Mo have larger electronegativities of 1.83 and 2.16 than those of Zr (1.33) and V (1.53). The substitutions of Fe/Mo for Zr/V in ZrV_2O_7 increase the electronegativity and decrease the effective negative charge on oxygen and the repelling force between oxygen atoms, which results in that oxygen-oxygen attractive forces cause the network collapse [26]. On the other hand, the partial substitutions of Fe/Mo for Zr/V in ZrV_2O_7 form Mo-O-V to reduce the symmetry of V-O-V, where the transverse motion of bridge O in V-O-V is responsible for the NTE of ZrV_2O_7 . V-O-V bond angle in ZrV_2O_7 is near 180° , which becomes smaller with increasing the substitutions of Fe/Mo for Zr/V in ZrV_2O_7 .

3.3 Lattice vibration

In order to further investigate the effects of substitutions of Fe/Mo for Zr/V in ZrV_2O_7

on lattice vibration, we also performed Raman characterization. Fig. 7 shows the Raman spectra of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with different x values from 0.0 to 0.9. Pure ZrV_2O_7 gives rise to characteristic Raman bands at about 231, 260, 373, 509, 776, 792, 953 and 988 cm^{-1} . The Raman modes at about 953 and 988 cm^{-1} and those at about 776 cm^{-1} and 792 cm^{-1} are assigned to symmetric and asymmetric stretching vibrations of the VO_4 tetrahedra. The Raman bands located between 300 and 550 cm^{-1} are attributed to symmetric and asymmetric bending of the VO_4 tetrahedra [20,27]. The lower wavenumber modes below 300 cm^{-1} may arise from the lattice modes.

As shown by Fig. 7, the Raman spectra change obviously with the contents of Fe^{3+} and Mo^{6+} , which reveals the interaction of polyhedra formed by substitution of Fe^{3+} and Mo^{6+} with the residing VO_4 tetrahedra in the building block. The first obvious change of the Raman spectra is the splittings of the asymmetric bending and stretching modes of VO_4 tetrahedra around 370 and 776 cm^{-1} for $x=0.1$. The splittings become larger with increasing with the content of Fe^{3+} and Mo^{6+} . The second distinct change of the Raman spectra is the appearance and shifts of the new Raman bands around 734, 837, 900 and 933 cm^{-1} when $x \geq 0.3$. These modes are attributed to the symmetric and asymmetric stretching vibrations of the MoO_4 tetrahedra. The third distinct change of the Raman spectra occurs when $x \geq 0.6$. The Raman bands around 988 cm^{-1} starts to split into two bands at about 974 and 986 cm^{-1} accompanied by progressive disappearance of the Raman band around 780 and 933 cm^{-1} . This is particularly obvious for $x > 0.7$. Similar phenomena are also observed for the Raman bands in the low wavenumber region.

Considering the XRD and Raman spectra changes with increasing the contents of Fe^{3+}

and Mo^{6+} , we conclude that (i) $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ remain the $3\times3\times3$ superstructure of ZrV_2O_7 at room temperature for $x=0.1 \sim 0.5$ but they present obvious distortion from ideal cubic structure, particularly for the samples with $x\geq 0.3$, due to the incorporation of $(\text{Fe}_{\text{Zr}})^-$ and $(\text{Mo}_{\text{V}})^+$; (ii) For $x\geq 0.6$, structure transition from cubic-to-monoclinic starts to occur. For $x=0.6 \sim 0.9$, the materials crystallize in a monoclinic structure.

In order to verify the interaction between VO_4 and MoO_4 tetrahedra, which could result in the intermediate states corresponding to some new Raman peaks, temperature dependent Raman spectra were performed for the samples with $x=0.3$ and 0.8 (Fig. 8). When $x=0.3$, the peaks at 896 and 932 cm^{-1} are gradually weakening or disappearing with increasing temperature, suggesting the intermediate states weaken with increasing temperature for low substitutions with weak interaction. For more substitution of $x=0.8$, the peak at 896 cm^{-1} almost remains the same with increasing temperature due to the strong interaction between the formed $(\text{Fe}_{\text{Zr}})^-$ and $(\text{Mo}_{\text{V}})^+$.

4. Conclusions

In summary, we developed a novel $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ material and investigated the effects of substitutions Fe/Mo for Zr/V in ZrV_2O_7 on the thermal expansion property. When the substitution of $x\leq 0.5$, the XRD patterns of the samples are consistent with the cubic ZrV_2O_7 . Strong interaction between the formed $(\text{Fe}_{\text{Zr}})^-$ and $(\text{Mo}_{\text{V}})^+$ could stabilize the crystal structure with higher substitutions of Fe^{3+} and Mo^{6+} . The sample with $x=0.9$ exhibited low thermal expansion property from 190 to 700 K , and the thermal expansion coefficient is low as $0.72\times 10^{-6}\text{ K}^{-1}$ at range of 140 to 400 K . The low thermal expansion mechanism of $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ is considered to relate to the distortion of crystal structure due to more substitutions of Fe/Mo for Zr/V in ZrV_2O_7 .

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References

- [1] J. Chen, F.F. Wang, Q.Z. Huang, L. Hu, X.P. Song, J.X. Deng, R.B. Yu, X.R. Xing, *Sci. Rep.* 3 (2013) 2458.
- [2] J. Yan, Y. Sun, Y.C. Wen, L.H. Chu, M.M. Wu, Q.Z. Huang, C. Wang, J.W. Lynn, Y.L. Chen, *Inorg. Chem.* 53 (2014) 2317.
- [3] W.J. Yao, X.X. Jiang, R.J. Huang, W. Li, C.J. Huang, Z.S. Lin, L.F. Li, C.T. Chen, *Chem. Commun.* 50 (2014) 13499
- [4] C. Closmann, A.W. Sleight, J.C. Hargarth, *J. Solid State Chem.* 139 (1998) 424.
- [5] F. Bridges, T. Keiber, P. Juhas, S.J.L. Billinge, L. Sutton, J. Wilde, G.R. Kowach, *Phys. Rev. Lett.* 112 (2014) 045505.
- [6] Q.Q. Liu, Z.Q. Yu, G.F. Che, J.L. Yao, X.J. Sun, X.N. Cheng, J. Yang, *Ceram. Int.* 40 (2014) 8195.
- [7] X.S. Liu, F.X. Cheng, J.Q. Wang, W.B. Song, B.H. Yuan, E.J. Liang, *J. Alloys Compd.* 553 (2013) 1.
- [8] N. Khosrovani, A.W. Sleight, *J. Solid State Chem.* 132 (1997) 355.
- [9] N. Khosrovani, V. Korthuis, A.W. Sleight, *Inorg. Chem.* 35 (1996) 485.

- [10] R.L. Withers, J.S.O. Evans, J. Hanson, A.W. Sleight, J. Solid State Chem. 137 (1998) 161.
- [11] R.L. Withers, Y. Tabira, J.S.O. Evans, I.J. King, A.W. Sleight, J. Solid State Chem. 157 (2001) 186.
- [12] S. Carlson, A.M.K. Andersen, J. Appl. Crystallogr. 34 (2001) 7.
- [13] U.L.C. Hemamala, F. El-Ghoussein, D.V.S. Muthu, A.M.K. Andersen, S. Carlson, L. Ouyang, M.B. Kruger, Solid State Commun. 141 (2007) 680.
- [14] V. Korthuis, N. Khosrovani, A.W. Sleight, J. Series Chem. Mater. 7 (1995) 412-417.
- [15] H.L. Yuan, B.H. Yuan, F. Li, E.J. Liang, Acta Phys. Sin. 22 (2012) 226502.
- [16] P.P. Sahoo, S. Sumithra, G. Madras, T.N.G. Row, Inorg. Chem. 50 (2011) 8774-8781.
- [17] Q.Q. Liu, J. Yang, X.J. Sun, X.N. Cheng, H. Tang, H.H. Li, Appl. Surf. Sci. 313 (2014) 41.
- [18] T. Hisashige, T. Yamaguchi, T. Tsuji, Y. Yamamura, J. Ceram. Soc. Jpn. 114 (2006) 607.
- [19] I. Yanase, T. Kojima, H. Kobayashi, Solid State Commun. 151 (2011) 595.
- [20] B.H. Yuan, H.L. Yuan, W.B. Song, X.S. Liu, Y.G. Cheng, M.J. Chao, E.J. Liang, Chin. Phys. Lett. 31 (2014) 076501.
- [21] B.H. Yuan, X.S. Liu, W.B. Song, Y.G. Cheng, E.J. Liang, M.J. Chao, Phys. Lett. A 378 (2014) 3397.
- [22] O. García-Moreno, A. Fernández, R. Torrecillas, J. Eur. Ceram. Soc. 30 (2010) 3219.
- [23] O. García-Moreno, A. Borrell, B. Bittmann, A. Fernández, R. Torrecillas, J. Eur. Ceram. Soc. 31 (2011) 1641.
- [24] A.M. Gindhart, C. Lind, M. Green, J. Mater. Res. 23 (2008) 210.
- [25] C. Dong, J. Appl. Cryst. 32 (1999) 838.

- [26] J.S.O. Evans, T.A. Mary, A.W. Sleight, J. Solid State Chem. 133 (1997) 580.
- [27] E.A. Petruska, D.V.S. Muthu, S. Carlson, A.M. Krogh Andersen, L. Ouyang, M.B. Kyuger, Solid State Commun. 150 (2010) 235.

Table list

Table 1. CTEs of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ calculated from temperature dependent XRD.

	CTE($\times 10^{-6}/\text{K}$)	CTE($\times 10^{-6}/\text{K}$)
	$\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$	$\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$
a	0.21	-0.40
b	3.85	-0.97
c	0.43	-1.22
V	4.25	-2.53

Table 2. CTEs of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ measured by dilatometer.

Sample	CTE($\times 10^{-6}/\text{K}$)	Temperature range(K)
ZrV_2O_7	-4.81	420-700
$\text{Zr}_{0.9}\text{Fe}_{0.1}\text{V}_{1.9}\text{Mo}_{0.1}\text{O}_7$	-2.21	450-700
$\text{Zr}_{0.7}\text{Fe}_{0.7}\text{V}_{1.7}\text{Mo}_{0.7}\text{O}_7$	-1.30	450-700
$\text{Zr}_{0.5}\text{Fe}_{0.5}\text{V}_{1.5}\text{Mo}_{0.5}\text{O}_7$	1.65	420-700
$\text{Zr}_{0.3}\text{Fe}_{0.7}\text{V}_{1.3}\text{Mo}_{0.7}\text{O}_7$	2.48	300-600
$\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$	1.86	300-600
$\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$	0.92	300-600

Figure list

Fig. 1 XRD patterns of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0.0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.8$, and 0.9 .

Fig. 2 Structure refinement results and schematics of building blocks of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0.0$ (a, b) and 0.3 (c, d) with XRD data at RT, where red balls present oxygen atoms.

Fig. 3 Indexing XRD pattern of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ by PowderX program.

Fig. 4 XRD patterns of $\text{Fe}_{0.8}\text{Zr}_{0.2}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ (a) and $\text{Fe}_{0.9}\text{Zr}_{0.1}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ (b) heated RT to 873 K.

Fig. 5 Dependence of lattice constants on temperature of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ (A) and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ (B). (C) Temperature dependences of cell volume of $\text{Zr}_{0.2}\text{Fe}_{0.8}\text{V}_{1.2}\text{Mo}_{0.8}\text{O}_7$ (V_1) and $\text{Zr}_{0.1}\text{Fe}_{0.9}\text{V}_{1.1}\text{Mo}_{0.9}\text{O}_7$ (V_2). (D) Relative length change of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with increasing temperature of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0, 0.1, 0.3, 0.5, 0.7, 0.8$, and 0.9 .

Fig. 6 Relative length change of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ for $x=0.0$ and 0.9 with increasing temperature.

Fig. 7 Raman spectra of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ at RT.

Fig. 8 Temperature dependent Raman spectra of $\text{Zr}_{1-x}\text{Fe}_x\text{V}_{2-x}\text{Mo}_x\text{O}_7$ with $x=0.3$ (a) and 0.8 (b).

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