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ABSTRACT

ZrV$_2$O$_7$ is a well-known isotropic negative thermal expansion (NTE) material. However, the NTE property of ZrV$_2$O$_7$ can only be observed in high temperatures above 375 K. In this paper, we report a facile method to break the superstructure of ZrV$_2$O$_7$ for realizing the NTE property of ZrV$_2$O$_7$ to room temperature by partial substitution of Mo for V atoms. The detailed structure information and the phase transition process are revealed by high-resolution synchrotron x-ray diffraction, neutron powder diffraction, and high pressure Raman spectral analyses. It is found that the incorporation of Mo prompts the V-O$_2$-V/Mo angles to expand from 160$^\circ$ to 180$^\circ$, which enables the NTE property at room temperature. Different from most open framework structures where NTE is dominated by low energy phonons, here several high energy phonon modes are found to have negative Gr"uneisen parameters and contribute to the negative thermal expansion.

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Negative thermal expansion (NTE) of certain type of materials is an active subject of research recently because negative thermal expansion (NTE) can be potentially used for many device applications and also there is a lot of interesting physics remaining to be explored. Until now, materials reported to display isotropic NTE are with the framework of oxides such as ZrW$_2$O$_8$,$^{2,3}$ ZrV$_2$O$_7$,$^4$ ReO$_3$-type fluorides ScF$_3$,$^5$ etc. Among these materials, the framework of oxides have obvious advantages of moderate NTE such as a wide temperature range, low cost, and ease of synthesis. ZrV$_2$O$_7$ is thermodynamically stable but it adopts a 3 $\times$ 3 $\times$ 3 superstructure at a low temperature and transforms to a 1 $\times$ 1 $\times$ 1 normal parent cubic structure above about 375 K. It displays a large positive and negative thermal expansion ($\alpha$ = $-7.1 \times 10^{-6}$ K$^{-1}$) below and above that temperature, respectively.$^6$ The high phase transition temperature hinders many practical applications.

Previously, many efforts have been made to reduce the structural phase transition temperature for ZrV$_2$O$_7$, including single site substitution of V by P, Mo, and W$^{6-11}$ or Zr by Hf and (Nb, Y)$^{12,13}$ and dual site substitution of Zr by Cu/P, Fe/P, etc.$^{14,15}$ The substitution method can slightly reduce the phase transition temperature and suppress the coefficients of positive and negative thermal expansion, but few attempts have succeeded in extending the NTE to well below RT. In some cases, the cubic structure could not be maintained, such as in the cases of W-substituted and Fe/Mo co-substituted ZrV$_2$O$_7$.$^{11,16}$ Single site substitution of Mo for V was considered by the solution combustion method previously but it was not effective in reducing the phase transition temperature.$^1$ Hence, it is still challenging to reduce the phase transition temperature and extend the NTE property of ZrV$_2$O$_7$-based materials to the room temperature.

The primary goal of our work is to reduce the phase transition temperature and extend the NTE of ZrV$_2$O$_7$ to well below room temperature (RT) by breaking the superstructure through Mo substitution for V. To realize this, we used a solid state reaction route followed by quenching of the samples. It is shown that the substitution of Mo for V could effectively break the superstructure and reduce the phase transition temperature. The onset of NTE for the sample of ZrV$_{1.5}$Mo$_{0.5}$O$_{7+\delta}$ is...
reduced to 225 K, below which it is actually a near-zero thermal expansion at least down to 123 K. Furthermore, the obtained samples with NTE covering RT enabled us to study the pressure-induced phase transition, amorphization, and phonon anharmonicity directly from the normal parent cubic structure, which was not possible previously. Previously, this could only be performed from the non-NTE superstructure. Pressure-dependent Raman spectra provide not only the information on pressure-induced phase transition and amorphization but also the mode Grünene parameters. It was believed that there was a link between the NTE and pressure-induced amorphization. The mode Grünene parameters provide useful insight into the thermal expansion mechanisms. This work provides not only a facile and effective method to widen the isotropic NTE temperature range of ZrV2O7 to meet practical applications, but also a deep understanding of the origins of NTE.

Sample materials of ZrV2–xMoxO7–δ (0 ≤ x ≤ 0.7) were synthesized by solid state reactions with the initial raw materials of ZrO2, MoO3, and V2O5. The mixtures were ground in an agate mortar for 2 h, and then pressed into cylindrical pellets. The pellets were sintered at 913 K for 4 h in a tubular furnace. After sintering, they were quenched in cold water and then dried at 393 K for 2 h in an oven. The samples were finally annealed at 673 K for 1 h.

The crystal structure was characterized by high-resolution synchrotron radiation x-ray diffraction (SXRD, Japan, ϵ = 0.495724 Å). The powder XRD was performed on a Rigaku (Japan, SmartLab 3kW) diffractometer with Cu Kα radiation. The relative length changes of the cylindrical samples were measured by a LINSEIS DIL L75 dilatometer at a heating and cooling rate of 5 K/min. The neutron powder diffraction and x-ray absorption near-edge structure data were collected at CSNS (GPPD beamline) and BSRF (1W1B beamline), respectively. High pressure Raman spectral measurements were carried out using a LabRAM HR Evolution Raman spectrometer (HORIBA Jobin Yvon S.A.A.) with 532 nm laser wavelength excitation. In the Raman experiments, the samples were kept in a diamond anvil with a small amount of ruby for pressure calibration and silicone oil was used as the pressure transmitting medium.

The purity of the as-synthesized samples was analyzed by XRD [Fig. 1(a)] and confirmed by SXRD (see the supplemental material Fig. S1). It indicates that the samples are pure phase ZrV2–xMoxO7–δ for x ≤ 0.5. Secondary phases appear when x ≥ 0.6 as indicated by the weak impurity peaks at 28.5° and 31.8°. The impurities are identified as ZrMo2O7 or ZrO2. The SXRD patterns of ZrV2–xMoxO7–δ (x = 0.1, 0.3, and 0.5) at room temperature could be best fitted with the cubic structure Pa-3 by Rietveld refinement, demonstrating that they maintain the cubic structure. The analyses of the XPS data for the Zr 3d, V 2p, and Mo 3d orbitals (Fig. S2) give rise to the binding energies of 182.40 and 185.00 eV for the Zr 3d3/2 and Zr 3d5/2 orbitals, 517.70 eV and 524.80 eV for the V 2p3/2 and V 2p5/2 orbitals, and 232.90 eV and 236.00 eV for the Mo 3d3/2 and Mo 3d5/2 orbitals, respectively. These results indicate that only tetravalent zirconium (Zr4+), pentavalent vanadium (V5+), and hexavalent molybdenum (Mo6+) exist in the samples of ZrV2–xMoxO7–δ. Since XANES is very sensitive to the change of chemical valence, we also carried out XANES analysis (Fig. S3). It is shown that no K-edge energy shift was observed in the Zr and Mo K-edge XANES spectra for ZrV2–xMoxO7–δ (x = 0.1, 0.3, and 0.5), suggesting no chemical valence change with the increase in the substitution amount of Mo for V atoms.

In order to observe the effect of substitution of Mo for V on the phase transition and thermal expansion properties, the relative length changes of bulk samples of ZrV2–xMoxO7–δ (0 ≤ x ≤ 0.5) were measured by a dilatometer and are shown in Fig. 1(b). It is obvious that the substitution of Mo for V shifts the phase transition to lower temperatures. ZrV2O7 displays a large positive thermal expansion at a low temperature and turns to NTE above 420 K by dilatometry measurement, which is consistent with previous reports. The phase transition temperature is reduced to about 350 and 300 K for x = 0.1 and 0.2, respectively. With a further increase of the Mo content, the phase transition temperature shifts successively to lower temperatures so that a wide range of NTE covering RT is realized for x ≥ 0.3.

To confirm the observed thermal expansion effect measured by dilatometry above, temperature-dependent XRD from 120 to 473 K was performed for each Mo-substituted sample (x = 0.1, 0.3, and 0.5) and the lattice constant at each temperature was calculated and is shown in Fig. 1(c). The results agree well with the dilatometry measurements, confirming that the Mo substitution can effectively reduce the phase transition temperature of ZrV2O7 and result in an intrinsic NTE over a wider temperature range. The
onset of NTE appears at about 350, 250, and 225 K, for \( x = 0.1, 0.3, \) and 0.5, respectively. The intrinsic coefficients of thermal expansion (CTE) for the \( \text{ZrV}_2\_x\text{Mo}_x\text{O}_{7.4} \) \((x = 0.1, 0.3, \) and 0.5\) are calculated to be \(-4.68 \times 10^{-6} \text{ K}^{-1} \) (375 K–473 K), \(-1.96 \times 10^{-6} \text{ K}^{-1} \) (250 K–473 K), and \(-1.95 \times 10^{-6} \text{ K}^{-1} \) (225 K–473 K), respectively. It is worth noting that the material of \( \text{ZrV}_{1.5}\text{Mo}_{0.5}\text{O}_7 \) at 375 K, suggesting that their

superstructure is broken below RT. It is noticed that the volumes of \( \text{ZrV}_{1.7}\text{Mo}_{0.3}\text{O}_{7.4} \) and \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) at 123 K have already exceeded their RT volumes and got close to the maximum values. These results indicate that the sample of \( \text{ZrV}_{1.7}\text{Mo}_{0.3}\text{O}_{7.4} \) retains the superstructure below the phase transition temperature, while \( \text{ZrV}_{1.7}\text{Mo}_{0.3}\text{O}_{7.4} \) and \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) do not due probably to the higher content of the Mo substitution for V atoms being able to break the superstructure even at a very low temperature (< 123 K).

To obtain the structure information and to experimentally verify the above analysis, we collected the NPD data for \( \text{ZrV}_{1.7}\text{Mo}_{0.3}\text{O}_{7.4} \) and \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) at the Chinese Spallation Neutron Source (CSNS), beam line GPPD (Fig. 2). The NPD patterns of both samples can be well refined with the normal parent structure \((Pa-3)\) with a high reliability \((\text{w}R_p = 0.0866, \text{R}_p = 0.0703 \text{ for } x = 0.3; \text{w}R_p = 0.0824, \text{R}_p = 0.0867 \text{ for } x = 0.5)\). If they were refined with the superstructure, no reliability could be obtained (Fig. S4). The refinement results for atomic positions, occupations, and bond lengths and angles are listed in Tables S1–S3. The structure refined results indicate that all the V-O2-V/Mo angles are 180° at RT; (b) Raman spectra of \( \text{ZrV}_{1.7}\text{Mo}_{0.3}\text{O}_7 \) at RT; (c) Raman spectra of \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_7 \) at different pressures; and (d) Raman mode frequency shifts as a function of pressure for \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_7 \) at RT.

Figure 3(a) presents the Raman spectra of \( \text{ZrV}_{2-x}\text{Mo}_x\text{O}_{7.4} \) \((x = 0, 0.1, 0.2, 0.3, 0.4, \) and 0.5\) at RT. With respect to the Raman spectrum of \( \text{ZrV}_2\text{O}_7 \), the most obvious changes in the Raman spectra of the Mo substituted samples are the appearance of a vibrational mode at about 902 cm\(^{-1}\), the broadening, and red shifts of most of the Raman peaks. The Raman mode at about 902 cm\(^{-1}\) is identified as the symmetric stretching vibrations of the MoO\(_4\) tetrahedra,\(^{24,25}\) whereas the broadening and red shifts of the Raman peaks result from the substitution-induced lattice distortion and softening of V–O bonds due to larger electronegativity of Mo\(^{6+}\) than V\(^{5+}\). The other Raman modes above 800 cm\(^{-1}\) and within 700–800 cm\(^{-1}\) are identified as symmetric and asymmetric stretching motions of the V–O bonds, while those within 400–600 cm\(^{-1}\), 200–400 cm\(^{-1}\), and below 200 cm\(^{-1}\) are attributed to the V–O symmetric bending/Zr–O stretching and V–O asymmetric bending and lattice modes, respectively.\(^{18,26}\) The progressive broadening and the red shifts of Raman peaks provide definite evidence of Mo incorporation into the lattice.

In order to get insight into the phonon anharmonicity and its contribution to the NTE of the Mo substituted \( \text{ZrV}_2\text{O}_7 \), we carried out a pressure dependent Raman spectroscopic study for \( \text{ZrV}_{2-x}\text{Mo}_x\text{O}_{7.4} \) [Fig. 3(b)] and \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) (Fig. S5). Both samples show Raman mode shifts with pressure as shown in Figs. 3(c), 3(d), and 3(e). With increasing pressure, most of the Raman modes shift to higher wave-numbers as expected due to shortening of the bonds upon pressuring but other Raman modes behave oppositely, such as the lattice mode at about 189 cm\(^{-1}\) and the symmetric stretching modes of VO\(_4\) tetrahedra above 800 cm\(^{-1}\) and the Mo–O stretching mode at about 902 cm\(^{-1}\). Besides, the peak intensity of the symmetric stretching mode of VO\(_4\) tetrahedra at about 987 cm\(^{-1}\) increases with respect to that of the asymmetric one at about 769 cm\(^{-1}\) with increasing pressure. It is inferred that the abnormal phenomena observed are related to the NTE of the Mo substituted samples. Detailed examination shows that the samples undergo two phase transitions with increasing pressure: from cubic (\( \alpha \)) to pseudo-tetragonal (\( \beta \)) phase transition and amorphization. The former is evidenced by the sudden changes of the Raman mode positions when the pressure is increased from 0.53 to

![FIG. 3. (a) Raman spectra of \( \text{ZrV}_{2-x}\text{Mo}_x\text{O}_{7.4} \) at RT; (b) Raman spectra of \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) at different pressures; and (c) and (d) Raman mode frequency shifts as a function of pressure for \( \text{ZrV}_{1.9}\text{Mo}_{0.1}\text{O}_{7.4} \) at RT.](image-url)
0.64 GPa for the sample of x = 0.3 and from 0.36 to 0.59 GPa for the sample of x = 0.5, while the latter is characterized by the vanishing of sharp peaks and appearance of broadened features in the Raman spectra above 3.45 GPa. 22,27

Since the mode Grüneisen parameter γi correlates with the coefficient of volume thermal expansion γV by γV = \frac{\partial a}{\partial T} \sum_i p_i \gamma_i \left(\frac{\partial a_i}{\partial T}\right) \quad \text{exp} \left(\frac{b_i}{k_B T}\right) \left[\exp \left(\frac{b_i}{k_B T}\right) - 1\right]^{-2}, it provides useful insight into the phonon anharmonicity and thermal expansion mechanisms, where a_i is the frequency of the ith mode, V is the molar volume, B_0 is the bulk modulus, and k_B is the Boltzmann constant. The mode Grüneisen parameters are obtained for both the cubic (x) and pseudo-tetragonal (β) phases of ZrV_{1.7}Mo_{0.3}O_{7+δ} (Table S4) and ZrV_{1.5}Mo_{0.5}O_{7+δ} (Table S5) according to γ_i = (x_i/\gamma_i)^{-1} (\partial a_i/\partial p), where P is the pressure and γ_i is the isothermal volume compressibility. In the calculation, the peak positions at ambient pressure were used for the x phase and those at 0.640 GPa (ZrV_{1.7}Mo_{0.3}O_{7+δ})/0.592 GPa (ZrV_{1.5}Mo_{0.5}O_{7+δ}) were used for the β phase. The compressibility γ_T = 5.8 × 10^{-2} GPa\(^{-1}\) for the x phase and 2.8 × 10^{-2} GPa\(^{-1}\) for the β phase of ZrV_2O_7 was used. 22,27 It can be seen from the tables that the symmetric stretching modes of VO_4 and MoO_4 tetrahedra possess negative Grüneisen parameters in both ZrV_{1.7}Mo_{0.3}O_{7+δ} and ZrV_{1.5}Mo_{0.5}O_{7+δ} samples besides the lowest frequency lattice modes. In most of the framework structure materials, the low frequency translational and vibrational modes contribute most to their negative thermal expansion. 22,27 Nevertheless, the high energy vibrational modes contribute considerably to the NTE as well here in the our case.

In summary, pure phase ZrV_{2-x}Mo_xO_{7+δ} (0 ≤ x ≤ 0.5) materials were synthesized by solid state reactions and their thermal expansion properties were investigated. It is found that the substitution of Mo for V atoms results in a large reduction of the superstructure to the parent cubic structure phase transition temperature and leads to a broadened NTE range. The onset of the NTE was reduced to 250 K and 225 K for ZrV_{2.0}Mo_{0.5}O_{7+δ} and ZrV_{2.0}Mo_{0.0}O_{7+δ}, respectively. ZrV_{1.5}Mo_{0.5}O_{7-δ} retains a near-zero thermal expansion below 225 K until the temperature of 120 K. It was demonstrated that the incorporation of Mo prompts the V-O2-V/Mo angles to straighten and favors breaking the superstructure. Pressure induced phase transition and amorphization were also revealed in the Mo substituted ZrV_2O_7. In contrast to previous framework structures where low frequency phonon modes mainly contribute to the NTE, several high frequency phonon modes are found to have negative Grüneisen parameters and hence contribute to the NTE as well in the structure. Our work not only provides a method of synthesizing materials with isotropic NTE covering the range of room temperature, but also develops the understanding of the mechanisms of NTE of materials.

See the supplementary material for the structure refinement results of ZrV_{2-x}Mo_xO_{7+δ}(x = 0.1, 0.3, and 0.5) and the valence state results including those of XPS and XANES, neutron powder diffraction, and pressure-dependent Raman spectra.

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