Pressure-dependence of the phase transitions and thermal expansion in zirconium and hafnium pyrovanadate

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Abstract

Low or negative thermal expansion (NTE) has been previously observed in members of the ZrP_2O_7 family at temperatures higher than their order-disorder phase transitions. The thermoelastic properties and phase behavior of the low temperature superstructure and high temperature negative thermal expansion phases of ZrV_2O_7 and HfV_2O_7 were explored via *in situ* variable temperature/pressure powder x-ray diffraction measurements. The phase transition temperatures of ZrV_2O_7 and HfV_2O_7 exhibited a very strong dependence on pressure (~ 700 K/GPa), with moderate compression suppressing the formation of their NTE phases below 513 K. Compression also reduced the magnitude of the coefficients of thermal expansion in both the positive and negative thermal expansion phases. Additionally, the high temperature NTE phase of ZrV_2O_7 was found to be twice as stiff as the low temperature positive thermal expansion superstructure (24 and 12 GPa respectively).

Keywords: thermal expansion, phase transitions, thermoelastic properties, zirconium pyrovanadate

1. Introduction

Negative thermal expansion (NTE) materials continue to receive considerable attention [1–3] due to fundamental interest in this unusual phenomenon and their potential application compensating for the positive thermal expansion (PTE) of other materials. Their use in composites [4–10] to provide enhanced dimensional stability, or an expansion match with other components, has been examined. However, thermal expansion mismatch between NTE and PTE materials in composites gives rise to internal stresses, which can be detrimental to the performance of the composite [9–13] as many NTE framework solids undergo phase transitions or changes in properties at low pressures. The combination of rich behavior upon modest compression and stresses arising from processing or thermal expansion mismatch motivates our studies of NTE materials under pressure [14–24].

While negative thermal expansion has been observed in a number of materials, many of them either exhibit NTE over a limited temperature range [25–27] or display highly anisotropic NTE [28–31]. Isotropic NTE over wide temperature range is especially interesting and has been observed in ZrW_2O_8 [32], ScF_3 [33], and other materials in these structural families [13, 18, 19, 32, 34, 35]. Isotropic

negative thermal expansion is also seen for some compositions in the ZrP_2O_7 family, but only at above ambient temperature [36–40]. ZrP_2O_7 itself does not exhibit NTE, but its thermal expansion dramatically decreases after undergoing a symmetry-increasing transition on heating [36, 41]. ZrV_2O_7 exhibits NTE above ~ 373 K at ambient pressure, where it has a ~ 8.8 Å cubic unit cell [36, 42]. Its low temperature (LT) form, which is a cubic $3 \times 3 \times 3$ superstructure of the high temperature (HT) NTE phase with a more ordered arrangement of V_2O_7 units [37, 43, 44], exhibits strong positive thermal expansion ($\alpha_{l,300\text{K}} = 24$ ppm·K⁻¹) [45]. A drawing of the subcell is shown in Figure 1. Heating the low temperature form leads to two phase transitions: the first gives rise to an incommensurate structure displaying PTE; the second leads to the high temperature NTE phase. Both occur within a narrow temperature range (~ 45 K) and are associated with large volume changes.

The behavior of ZrV_2O_7 under pressure has previously been studied at ambient temperature [46, 47]. On compression to 1.38 GPa, ZrV_2O_7 transforms to a phase with orthorhombic symmetry, and above 4 GPa it amorphizes [46, 47]. The low temperature form of cubic ZrV_2O_7 ($\kappa_T = 17$ GPa) was reported to be much softer than other members of the ZrP_2O_7 family at ambient temperature ($\kappa_T(\text{ZrP}_2\text{O}_7, \text{TiP}_2\text{O}_7) \simeq 40$ GPa) [46], and is much softer than previously studied ZrW_2O_8 family members ($\kappa_T = 41$ –74 GPa) [14, 15, 34, 48, 49]. However, ZrV_2O_7 only adopts a structure that supports NTE at above room temperature, and no high pressure studies have been performed on this phase. In this paper, the phase behavior,

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Figure 1: Structure of the high temperature (NTE) phase of ZrV_2O_7 . The ZrO_6 octahedra and VO_4 tetrahedra are yellow and blue respectively.

thermal expansion and elastic properties of ZrV_2O_7 and HfV_2O_7 are examined at pressures/temperatures between 0 - 310 MPa and 300 - 525 K; a regimen which is well matched to likely applications for NTE solids.

2. Methods

2.1. Syntheses

Zirconium and hafnium pyrovanadate were synthesized via a previously described solid-state route [36]. Zirconyl chloride hydrate (Alfa Aesar, Ward Hill, MA) and hafnium oxychloride hydrate (Alfa Aesar, Ward Hill, MA) were mixed with a $\geq 5\%$ stoichiometric excess of ammonium metavanadate (Fisher Scientific, Waltham, MA). Samples were heated at 1023 K in ~ 24 hr increments, sand-quenched, and reground. Heat treatments were repeated until the samples were essentially phase pure. Laboratory x-ray powder diffraction was used to verify the identity and purity of the final products.

2.2. Sample Environment and X-ray Data Collection

High pressure diffraction patterns were collected at beam line 11-ID-B of the Advanced Photon Source using 58.65 keV (0.2114 Å) x-rays, a sample to detector distances of ~ 87 cm and a PerkinElmer amorphous silicon 2D detector. A previously described variable temperature/pressure sample environment was used to access temperatures between 298 and 513 K and pressures upto 310 MPa [14, 15, 50]. Two different data collection schemes were utilized. In the first, samples were initially compressed to 310 MPa in 103 MPa increments, decompressed to 257 MPa, then decompressed to 52 MPa in 103 MPa increments. In the second, samples were initially compressed to 155 MPa in 52 MPa increments, decompressed to 129 MPa, then decompressed to 26 MPa in 52 MPa increments. In both cases, samples were subsequently heated to the next temperature, where the same compression/decompression scheme was used.

Ambient pressure/variable temperature x-ray scattering data were also collected at beamline 11-ID-B of the

Figure 2: Rietveld fit using the high temperature $\text{Pa}\bar{3}$ model for ZrV_2O_7 XRD pattern collected at room temperature and 310 MPa.

Advanced Photon Source using 58.26 keV (0.2128 Å) x-rays. Powdered samples were loaded into Kapton capillaries. Temperatures between 100 and 500 K were accessed using an Oxford Cryosystems Cryostream. Samples were initially cooled to 100 K, then heated to 500 K at $1 \text{ K}\cdot\text{min}^{-1}$.

2.3. Diffraction Data Analysis

Rietveld analysis of the data [51–53] was performed after reduction of images to one-dimensional patterns [50, 54, 55]. A structural model for the high temperature phase, taken from Khosrovani et al. [37], was used in these analyses. Lattice constants were obtained from refinements where a background function (10 term shifted Chebyshev), scale factor, unit cell edge, 4 profile coefficients, and isotropic atomic displacement parameters for Zr/Hf and V were varied. Refinement of atomic positions and oxygen atomic displacement parameters could not be performed using the available data. Rietveld analyses of data recorded in this sample environment can be problematic due to poor sampling statistics associated with the small volume of illuminated sample, high background levels due to the significant amount of material in the beam path, and partial shadowing at low Q by the internal beam stop. The resolution of the data is also limited by the size and pixel size of the detector. A representative fit using the high temperature subcell model for ZrV_2O_7 is shown in Figure 2. Analyses using the much more complex room temperature superstructure were unsuccessful, due to the limited quality of the available data. Previous studies have shown that the supercell $\rightarrow$ incommensurate and incommensurate $\rightarrow$ subcell transitions are associated with large increases in lattice constant, and that NTE occurs only in the high temperature phase. The pressures and temperatures at which these phase transitions occur were estimated based on steep changes in volume and the onset of NTE [36–38, 42, 45].

Figure 3: Variation of lattice parameters for ZrV_2O_7 with temperature at different pressures: 26 MPa (red), 52 MPa (goldenrod), 78 MPa (blue), 103 MPa (magenta), 129 MPa (cyan), 155 MPa (black), 206 MPa (purple), 258 MPa (dark-green), and 310 MPa (gray).

3. Results and Discussion

3.1. Pressure Dependence of the Phase Transitions

The dependence of the lattice parameters for ZrV_2O_7 on temperature at different pressures are shown in Figure 3 and in Supporting Information Tables I-III. The steep increases in volume associated with the supercell $\rightarrow$ incommensurate and incommensurate $\rightarrow$ subcell transitions are both shifted to significantly higher temperatures as the pressure is increased. The onset of NTE was shifted by ~ 38 K in ZrV_2O_7 and ~ 36 K in HfV_2O_7 upon increasing sample pressure from 52 to 103 MPa and later measurements on ZrV_2O_7 , which included additional temperature points between 473 and 513 K, revealed that at 155 MPa, the onset of NTE occurs at 497 K, an increase of ~ 80 K above the transition temperature at 52 MPa. Large changes in the supercell $\rightarrow$ incommensurate phase transition temperature are also observed for both ZrV_2O_7 and HfV_2O_7 on compression.

The phase behavior of ZrV_2O_7 upon compression and heating is summarized in Figure 4. The phase at each point in pressure temperature space was assigned based on the variation of the lattice constant with temperature at each pressure as shown in Figure 3: points below the first large volume change at a given pressure were assigned to the low temperature (LT) phase; points between the first and second large volume changes were assigned to the incommensurate phase; points above the second large volume change, where the onset of NTE was observed, were assigned to the high temperature (HT) NTE phase. Supercell/incommensurate and incommensurate/subcell phase boundaries were drawn to separate the phases. The slopes of the phase boundaries $(\frac{dT}{dP})_{\text{LT} \rightarrow \text{inc.}}$ and $(\frac{dT}{dP})_{\text{inc.} \rightarrow \text{HT}}$ were estimated to be $\sim 640 \text{ K}\cdot\text{GPa}^{-1}$ and $\sim 740 \text{ K}\cdot\text{GPa}^{-1}$ respectively. These transitions are approximately an order of magnitude more pressure-sensitive than those observed in many materials, including perovskites (~ 10 - $80 \text{ K}\cdot\text{GPa}^{-1}$) [56]; however, they are comparable to those observed in ScF_3 and $\text{Sc}_{1-x}\text{Al}_x\text{F}_3$ (400 - $500 \text{ K}\cdot\text{GPa}^{-1}$), which

Figure 4: Pressure-temperature phase diagram of ZrV_2O_7 . The LT phase is indicated by blue circles, incommensurate by goldenrod diamonds, and HT by red triangles.

are essentially A-site vacant perovskites [19, 33].

For first order transitions, the slope of the pressure temperature phase boundary is related to the volume and entropy changes associated with the transition by the Clapeyron equation [57]:

$$\frac{dP}{dT} = \frac{\Delta_{trs}\bar{S}}{\Delta_{trs}\bar{V}} \quad (1)$$

If we assume that this equation is approximately applicable to our system, we can use molar volume changes estimated from our variable temperature XRD measurements, conducted at ambient pressure between 100 and 500 K (Figure 5 and Supporting Information Table IV), along with previously reported calorimetry-derived $\Delta_{trs}S$ for the two phase transitions ($0.41 \pm 0.01 \text{ J}/(\text{K}\cdot\text{mol})$ and $0.73 \pm 0.05 \text{ J}/(\text{K}\cdot\text{mol})$ respectively) [45] to independently estimate the phase boundary slope for each transition. The change in molar volume for each transition was taken to be the difference between the beginning and end of each steep increase in volume. This results in estimates for $(\frac{dT}{dP})$, of $\sim 740 \text{ K}\cdot\text{GPa}^{-1}$ for the supercell $\rightarrow$ incommensurate and $\sim 590 \text{ K}\cdot\text{GPa}^{-1}$ for the incommensurate $\rightarrow$ subcell transitions, which are remarkably close to those determined directly from the high pressure measurements.

3.2. Phase-Dependent Variation in Compressibility with Temperature

The isothermal bulk modulus is defined in the equation below [57]:

$$\kappa_T \equiv - \left(\frac{\partial P}{\partial \ln V} \right)_T \quad (2)$$

Linear regression to $\ln(\text{Volume})$ versus pressure data was used to determine bulk moduli (Supporting Information Figure 2). Bulk moduli for ZrV_2O_7 and HfV_2O_7 at temperatures between room temperature and 513 K are shown in Figure 6 and Supporting Information Tables V-VII. Average room temperature bulk moduli of ZrV_2O_7 and HfV_2O_7 derived from our measurements are lower than

Figure 5: Lattice parameters of ZrV_2O_7 between 300 and 380 K obtained from ambient pressure XRD measurements.

Figure 6: Bulk moduli of ZrV_2O_7 calculated between 25 and 155 MPa.

that previously reported for ZrV_2O_7 (17 GPa) [46]. As a substantially broader pressure range (0-1.38 GPa) was used to determine the previously reported ambient temperature bulk modulus [46] and pressure-induced stiffening is a common phenomenon in solids [58, 59], a more relevant comparison might be obtained from recalculating the bulk modulus using data that lies within a comparable pressure range. Recalculation of the bulk modulus using only data between 80 and 290 MPa [46], resulted in a $\sim 50\%$ drop in magnitude to 8.7 GPa.

Upon heating, the bulk modulus for ZrV_2O_7 ($\kappa_{25-155\text{MPa}}$) drops $\sim 46\%$ in the regime where the incommensurate phase is present. A comparable softening is observed in HfV_2O_7 . Upon heating to 513 K, where the NTE phase is present, the stiffness of both materials increases by over 100% relative to room temperature. The twofold increase in stiffness observed upon heating was not anticipated, as most materials soften upon heating [60–62]. In previous studies of open framework NTE materials, significant softening upon heating was observed in ZrW_2O_8 and HfW_2O_8 [14, 15], while slight stiffening occurred in ZrMo_2O_8 [14], $\text{Y}_x\text{Sc}_{1-x}\text{F}_3$ [20], and $\text{Al}_x\text{Sc}_{1-x}\text{F}_3$ [19]. The cause of the increase in elastic stiffness of the **HT** phase as compared to the **LT** structure is unknown, but may be due to differences in the orientational ordering of V_2O_7 units between the two phases.

3.3. Pressure-Induced Reductions in Coefficient of Thermal Expansion

The temperature dependence of the bulk modulus and the pressure dependence of the coefficient of thermal expansion (CTE) are related as described in Equation 3 [60]:

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{1}{\kappa_T^2} \left(\frac{\partial \kappa_T}{\partial T}\right)_P \quad (3)$$

The pressure dependence of the linear CTEs of ZrV_2O_7 and HfV_2O_7 are shown in Figure 7 and Supporting Information Figure 1. The CTE of the **LT** phase of ZrV_2O_7 at 52 MPa (24 ppm/K) matches the ambient pressure CTE reported in previous literature [45]; the high temperature CTE at 26 MPa (-7.2 ppm/K) is also relatively close to the previously reported ambient pressure CTE (-6.8 ppm/K) [42]. A substantial reduction in the magnitude of both CTEs was observed upon compression. The reduction in CTE appears to be a byproduct of the extremely pressure-sensitive phase transitions that occur in ZrV_2O_7 . The CTE of the **HT** phase becomes less negative ($\sim 85\%$) upon compression, as increasing the pressure eventually drives ZrV_2O_7 back through the subcell $\rightarrow$ incommensurate transition, which is associated with both large changes in volume and positive thermal expansion. Similarly, since the supercell $\rightarrow$ incommensurate temperature increases with pressure, compression of the **LT** phase forces ZrV_2O_7 further away from this transition and the large increase in volume associated with it, resulting in a $\sim 35\%$ drop in CTE between 52 and 310 MPa. The reduction in the CTE

Figure 7: Variation of ZrV_2O_7 linear CTEs with pressure. ZrV_2O_7 CTEs were calculated between 298 and 363K for the LT phase (top) and 479-513 K for the HT phase (bottom).

of the supercell phase upon compression, 9 ppm/K, is even larger than the change in CTE observed in HfW_2O_8 over a broader pressure range [15]. In HfV_2O_7 , noticeable hysteresis in volume upon compression and decompression at room temperature resulted in erroneously lowered supercell CTEs at pressures measured on decompression (Supporting Information Figures 1-2). While overall, a noticeable reduction in the CTE was observed upon compression much like ZrV_2O_7 , quantitative statements about the extent of this reduction cannot be made definitely due to the large errors associated with these CTEs.

4. Conclusions

Variable temperature/pressure measurements revealed that temperatures at which the supercell $\rightarrow$ incommensurate and incommensurate $\rightarrow$ subcell transitions occur in ZrV_2O_7 and HfV_2O_7 are strongly pressure-dependent. The pressure-sensitivity observed was even more pronounced in these materials than in other open framework materials such as ScF_3 [19, 33]. The CTEs of both the HT and LT phases were strongly pressure-dependent. On heating, elastic softening was observed at temperatures close to the transition to the incommensurate phase prior to considerable stiffening in the HT phase. However, unlike ZrW_2O_8 and HfW_2O_8 [14, 15], compression elevates transition temperatures. The drop in magnitude of the CTE

on compression of the LT phase arises primarily because the LT $\rightarrow$ incommensurate transition, and its associated volume increase, occurs at higher temperatures. The precise origin of the considerable stiffening seen on going from the LT to HT structures is unknown, but it is presumably associated with orientational disordering within the V_2O_7 units.

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References

- [1] C. P. Romao, K. J. Miller, C. A. Whitman, M. A. White, B. A. Marinkovic, Negative Thermal Expansion (Thermomimetic) Materials, Vol. 4, Elsevier, Oxford, 2013, pp. 128–151.
- [2] C. Lind, Materials 5 (6) (2012) 1125–1154.
- [3] J. Chen, L. Hu, X. Xing, Negative thermal expansion in functional materials: controllable thermal expansion by chemical modifications, Chem. Soc. Rev. 44 (2015) 3522–3567.
- [4] E. Della Gaspera, R. Tucker, K. Star, E. H. Lan, Y. S. Ju, B. Dunn, ACS Appl. Mater. Interfaces 5 (21) (2013) 10966–74.
- [5] K. Takenaka, Science and Technology of Advanced Materials 13 (1) (2012) 013001.
- [6] C. Lind, M. R. Coleman, L. C. Kozy, G. R. Sharma, Phys. Status Solidi. B 248 (1) (2011) 123–129.
- [7] A. Chandra, W. H. Meyer, A. Best, A. Hanewald, G. Wegner, Macromol. Mater. Eng. 292 (3) (2007) 295–301.
- [8] P. Lommens, C. De Meyer, E. Bruneel, K. De Buysser, I. Van Driessche, S. Hoste, Journal of The European Ceramic Society 25 (16) (2005) 3605–3610.
- [9] D. K. Balch, D. C. Dunand, Metall. Mater. Trans. A 35A (2004) 1159–1165.
- [10] S. Yilmaz, J. Phys.: Condens. Matter 14 (2002) 365–375.
- [11] Y. Wu, M. L. Wang, Z. Chen, N. H. Ma, H. W. Wang, Journal of Materials Science 48 (7) (2013) 2928–2933.
- [12] S. Yilmaz, D. C. Dunand, Compos. Sci. Technol. 64 (12) (2004) 1895–1898.
- [13] C. R. Morelock, M. R. Suchomel, A. P. Wilkinson, J. Appl. Crystallogr. 46 (3).
- [14] L. C. Gallington, K. W. Chapman, C. R. Morelock, P. J. Chupas, A. P. Wilkinson, Phys. Chem. Chem. Phys. 15 (45) (2013) 19665–19672.
- [15] L. C. Gallington, K. W. Chapman, C. R. Morelock, P. J. Chupas, A. P. Wilkinson, J. Appl. Phys. 115 (5) (2014) 053512.
- [16] T. Varga, A. P. Wilkinson, A. C. Jupe, C. Lind, W. A. Bassett, C.-S. Zha, Phys. Rev. B 72 (2005) 024117–(1–10).
- [17] T. Varga, A. P. Wilkinson, C. Lind, W. A. Bassett, C.-S. Zha, Solid State Commun. 135 (2005) 739–744.
- [18] J. C. Hancock, K. W. Chapman, G. J. Halder, C. R. Morelock, B. S. Kaplan, L. C. Gallington, A. Bongiorno, C. Han, S. Zhou, A. P. Wilkinson, Chem. Mater. 27 (11) (2015) 3912–3918.
- [19] C. R. Morelock, L. C. Gallington, A. P. Wilkinson, J. Solid State Chem. 222 (2015) 96–102.
- [20] C. R. Morelock, B. K. Greve, L. C. Gallington, K. W. Chapman, A. P. Wilkinson, J. Appl. Phys. 114 (21) (2013) 213501.
- [21] M. Cetinkol, A. P. Wilkinson, C. Lind, Phys. Rev. B 79 (22) (2009) 224118–10.

- [22] T. Varga, A. P. Wilkinson, C. Lind, W. A. Bassett, C.-S. Zha, *Phys. Rev. B* 71 (2005) 214106 (1–8).
- [23] T. Varga, A. P. Wilkinson, C. Lind, W. A. Bassett, C.-S. Zha, *J. Phys.: Condens. Matter* 17 (2005) 4271–4283.
- [24] T. Varga, A. P. Wilkinson, J. D. Jorgensen, S. Short, *Solid State Sciences* 8 (2006) 289–295.
- [25] T. Chatterji, T. C. Hansen, M. Brunelli, P. F. Henry, *Appl. Phys. Lett.* 94 (24) (2009) 241902.
- [26] M. Azuma, W.-t. Chen, H. Seki, M. Czapski, S. Olga, K. Oka, M. Mizumaki, T. Watanuki, N. Ishimatsu, N. Kawamura, S. Ishiwata, M. G. Tucker, Y. Shimakawa, J. P. Attfield, *Nat. Commun.* 2 (2011) 347.
- [27] Y. W. Long, N. Hayashi, T. Saito, M. Azuma, S. Muranaka, Y. Shimakawa, *Nature* 458 (7234) (2009) 60–U3.
- [28] A. L. Goodwin, M. Calleja, M. J. Conterio, M. T. Dove, J. S. O. Evans, D. A. Keen, L. Peters, M. G. Tucker, *Science* 319 (5864) (2008) 794–797.
- [29] J. S. O. Evans, T. A. Mary, A. W. Sleight, *J. Solid State Chem.* 137 (1998) 148–160.
- [30] J. S. O. Evans, T. A. Mary, A. W. Sleight, *J. Solid State Chem.* 133 (1997) 580–583.
- [31] G. Lenain, H. A. McKinsty, S. Y. Limaye, A. Woodward, *Mat. Res. Bull.* 19 (1984) 1451–1456.
- [32] J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian, A. W. Sleight, *Chem. Mater.* 8 (1996) 2809–2823.
- [33] B. K. Greve, K. L. Martin, P. L. Lee, P. J. Chupas, K. W. Chapman, A. P. Wilkinson, *J. Am. Chem. Soc.* 132 (44) (2010) 15496–15498.
- [34] C. Lind, A. P. Wilkinson, Z. Hu, S. Short, J. D. Jorgensen, *Chem. Mater.* 10 (1998) 2335–2337.
- [35] C. R. Morelock, L. C. Gallington, A. P. Wilkinson, *Chem. Mater.* 26 (5) (2014) 1936–1940.
- [36] V. Korthuis, N. Khosrovani, A. W. Sleight, N. Roberts, R. Dupree, W. W. Warren, *Chem. Mater.* 7 (1995) 412–417.
- [37] N. Khosrovani, A. Sleight, T. Vogt, *J. Solid State Chem.* 132 (1997) 355–360.
- [38] C. Turquat, C. Muller, E. Nigrelli, C. Leroux, J.-L. Soubeyroux, G. Nihoul, *Eur. Phys. J. AP* 10 (2000) 15–27.
- [39] H. Kirchner, K. Merz, W. Brown, *J. Am. Ceram. Soc.* 46 (1963) 137–141.
- [40] K. M. White, P. L. Lee, P. J. Chupas, K. W. Chapman, E. A. Payzant, A. C. Jupe, W. A. Bassett, C. S. Zha, A. P. Wilkinson, *Chem. Mater.* 20 (11) (2008) 3728–3734.
- [41] T. Ota, I. Yamai, *J. Mater. Sci.* 22 (1987) 3762–3764.
- [42] D. Craig, F. Hummel, *J. Am. Ceram. Soc.* 55 (1972) 532.
- [43] J. Evans, J. Hanson, A. Sleight, *Acta Cryst. B* 54 (1998) 705–713.
- [44] R. L. Withers, J. S. O. Evans, J. Hanson, A. W. Sleight, *J. Solid State Chem.* 137 (1998) 161–167.
- [45] Y. Yamamura, A. Horikoshi, S. Yasuzuka, H. Saitoh, K. Saito, *Dalton Trans.* 40 (10) (2011) 2242–2248.
- [46] S. Carlson, A. Krogh Andersen, *J. Appl. Cryst.* 34 (2001) 7–12.
- [47] T. Sakuntala, A. K. Arora, V. Sivasubramanian, R. Rao, S. Kalavathi, S. K. Deb, *Phys. Rev. B* 75 (17) (2007) 174119.
- [48] J. D. Jorgensen, Z. Hu, S. Teslic, D. N. Argyriou, S. Short, J. S. O. Evans, A. W. Sleight, *Phys. Rev. B* 59 (1999) 215–225.
- [49] J. D. Jorgensen, Z. Hu, S. Short, A. W. Sleight, J. Evans, *J. Appl. Phys.* 89 (2001) 3184–3188.
- [50] A. P. Wilkinson, C. R. Morelock, B. K. Greve, A. C. Jupe, K. W. Chapman, P. J. Chupas, C. Kurtz, *J. Appl. Crystallogr.* 44 (5) (2011) 1047–1053.
- [51] A. Larson, R. Von Dreele, GSAS - General Structure Analysis System, Report LA-UR-86-748, Los Alamos Laboratory, 1987.
- [52] S. Vogel, *J. Appl. Crystallogr.* 44 (4) (2011) 873–877.
- [53] B. H. Toby, *J. Appl. Crystallogr.* 34 (2001) 210–213.
- [54] G. Jennings, QXRD - Readout Software for Flat Panel X-Ray Detectors (unpublished).
- [55] A. Hammersley, FIT2D: An Introduction and Overview, Tech. rep., ESRF (1997).
- [56] G. A. Samara, T. Sakudo, K. Yoshimitsu, *Phys. Rev. Lett.* 35 (26) (1975) 1767–1769.
- [57] D. A. McQuarrie, J. D. Simon, University Science Books, Sausalito, California, 1997.
- [58] D. L. Decker, *J. Appl. Phys.* 36 (1965) 157–161.
- [59] K. Brister, *Rev. Sci. Instr.* 68 (1997) 1629–1647.
- [60] O. Anderson, *Equations of state of solids for geophysics and ceramic science*, Oxford University Press, Oxford, 1995.
- [61] L. A. Girifalco, *Statistical mechanics of solids*, Vol. 58, Oxford University Press, 2003.
- [62] J. Garai, A. Laugier, *J. Appl. Phys.* 101 (2) (2007) 023514.

The temperature at which ZrV_2O_7 transforms to a phase displaying negative thermal expansion is strongly pressure dependent. The high temperature form of ZrV_2O_7 is elastically stiffer than the low temperature form.