

## PHASE TRANSITION OF NEGATIVE THERMAL EXPANSION $Zr_{1-x}Hf_xW_2O_8$ SOLID SOLUTIONS\*

*N. Nakajima*<sup>1</sup>, *Y. Yamamura*<sup>2</sup> and *T. Tsuji*<sup>1\*\*</sup>

<sup>1</sup>School of Materials Science,

<sup>2</sup>Center for New Materials, Japan Advanced Institute of Science and Technology, 1-1 Asahidai, Tatsunokuchi, Ishikawa 923-1292, Japan

### Abstract

A powder X-ray diffraction experiment was performed on cubic  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.50$  and  $0.75$ ) solid solutions from 90 to 560 K. The lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  at 121 K decreased linearly with increasing Hf contents, due to smaller ionic radius of hafnium than that of zirconium. Transition temperatures due to  $\alpha$ - $\beta$  structural phase transition increased with increasing Hf contents, reflecting the decrease of lattice free volume related to the orientation of unshared vertex of  $WO_4$ . Anomaly in the heat capacity of  $Zr_{0.5}Hf_{0.5}W_2O_8$  was observed around 450 K which was 9 K lower than that by X-ray diffraction method. Transition entropy of  $Zr_{0.5}Hf_{0.5}W_2O_8$  was  $2.1 \text{ J mol}^{-1} \text{ K}^{-1}$ , consistent with those of  $ZrW_2O_8$  and  $HfW_2O_8$ . This consistent entropy supports that  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0-1.0$ ) has the same order-disorder phase transition mechanism.

**Keywords:** heat capacity,  $HfW_2O_8$ , negative thermal expansion, phase transition,  $ZrW_2O_8$

### Introduction

$ZrW_2O_8$  has received considerable attention in the past several years because of its isotropic negative thermal expansion over a wide temperature range from 0.3 to 1050 K [1–3]. The crystal structure of  $ZrW_2O_8$  has a framework structure that is characterized by linkage of corner shared  $WO_4$  tetrahedron and  $ZrO_6$  octahedron. Those polyhedrons share the oxygen atoms at the vertices of the polyhedron each other except one of oxygen atoms of a unit. The framework structure and the libration of the  $WO_4$  unit with the unshared vertex result in the nature of negative thermal expansion [4, 5].  $ZrW_2O_8$  undergoes an  $\alpha$ - $\beta$  structural phase transition at about 440 K from an acentric to a centric structure with increasing temperature. The  $\alpha$ - $\beta$  structural phase transition is related to the orientation of the unshared vertex of  $WO_4$  unit and considered to be order-disorder type [1, 2].

\* This paper was presented at the Second International Symposium on the New Frontiers of Thermal studies of Materials, Yokohama, Japan, November, 2001.

\*\* Author for correspondence: E-mail: [tsuji@jaist.ac.jp](mailto:tsuji@jaist.ac.jp)

$HfW_2O_8$  having the same crystal structure as  $ZrW_2O_8$  shows a negative thermal expansion. It is well known that zirconium and hafnium ions resemble each other in chemical property. However, the ionic radius of hafnium is slightly smaller than that of zirconium and the atomic mass of hafnium is about twice heavier than that of zirconium. Many studies were available on those of  $ZrW_2O_8$ , but only negative thermal expansion data by thermomechanical analysis (TMA) were reported for  $HfW_2O_8$  and  $Zr_{0.5}Hf_{0.5}W_2O_8$  [6].

Recently we have reported the study of negative thermal expansion and phase transition on  $ZrW_2O_8$  and  $HfW_2O_8$  by X-ray diffraction and calorimetric measurements [7, 8]. Heat capacity data showed that phase transition temperature of  $HfW_2O_8$  was about 25 K higher than that of  $ZrW_2O_8$  and both transition entropies were the same. The fact of the same entropy supports that phase transitions of  $ZrW_2O_8$  and  $HfW_2O_8$  are of the same order-disorder type, where two  $WO_4$  tetrahedra on [111] diagonal in the unit cell have only two conformations in a concerted manner.

In this paper we report the effects of Hf contents on the lattice parameters and phase transition of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solutions by X-ray diffraction method and on phase transition of  $Zr_{0.5}Hf_{0.5}W_2O_8$  by calorimetric measurement.

## Experimental

$Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solutions were synthesized by solid-state reaction.  $ZrO_2$ ,  $HfO_2$  and  $WO_3$  were mixed at the required proportion thoroughly in an agate mortar and pressed in a steel die to form pellets. The pellets were then calcined at 1473 K for 12 h in air and rapidly cooled down to room temperature. After grinding the quenched pellets to get homogeneous solid solution, the resulting powders were pressed into pellets. The pellets were sintered at 1473 K for 12 h and quenched in liquid nitrogen to avoid decomposition of solid solution.

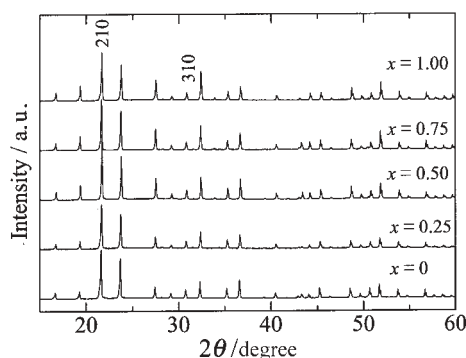
The samples of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solutions were characterized by X-ray powder diffractometer using  $CuK_\alpha$  radiation with 40 kV–200 mA (RINT 2500V, Rigaku), having low and high temperature attachments capable of controlling temperature within  $\pm 1$  K. The XRD data were collected by a step scanning method in the  $2\theta$  range from 10 to  $100^\circ$  with a step width of  $0.01^\circ$  and a scan time of 0.7 s. The powder patterns were obtained at about 35 temperatures from 90 to 560 K in a vacuum environment. Temperature was kept at constant at each temperature. For XRD, the sample was on copper plate and temperature was controlled by K-type thermocouple attached to the back of copper plate. We measured temperature at the surface of the sample by using another K-type thermocouple thermometer and then a correct temperature was used in this study.

The heat capacity of  $Zr_{0.5}Hf_{0.5}W_2O_8$  was measured by an adiabatic scanning calorimeter (ASC) at temperatures from 350 to 550 K. Details of the apparatus and operation of the ASC have been described elsewhere [7]. The crushed samples of  $Zr_{0.5}Hf_{0.5}W_2O_8$  were loaded into a quartz ampul as a calorimeter vessel and sealed with small amounts of helium gas (20 kPa at room temperature) to assist thermal equilibration within the ampul. The amount of the sample used for the measurement

was about 16 g. Before heat capacity measurement, the ampul with the sample was annealed at about 800 K for 1 h, in order to remove the quenching effects in the sample preparation. The heating rate chosen in this study was about  $1.8 \text{ K min}^{-1}$ . A preliminary heat capacity measurement of sapphire using the ASC showed that a precision and an accuracy of the calorimeter were within  $\pm 2\%$  and  $\pm 2\%$ , respectively, in comparison with the reliable data of sapphire [9].

## Results and discussion

All samples of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solutions were characterized to be of a single phase by a powder X-ray diffraction method. The X-ray diffraction profiles of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solutions at 121 K are shown in Fig. 1, together with those of  $ZrW_2O_8$  and  $HfW_2O_8$  by our previous work [8]. The X-ray diffraction profiles of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) are very similar to those of  $ZrW_2O_8$  and  $HfW_2O_8$ . The 310 peak of all samples shown in Fig. 1 disappeared above phase transition temperature. The diffraction peaks in the X-ray profiles were assigned by referring to the previous work on  $ZrW_2O_8$  by Sleight's group [2]. Lattice parameters of these samples were determined using about 40 diffraction peaks between 40 and 100 by a least-square calculation after correcting  $2\theta$  with Nelson–Rieley's method [10].



**Fig. 1** X-ray diffraction patterns of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.50$  and  $0.75$ ) at 121 K, together with those of  $ZrW_2O_8$  and  $HfW_2O_8$  by our previous work [8]

Figure 2 shows the lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) solid solution at 121 K, together with our previous data of  $ZrW_2O_8$  and  $HfW_2O_8$  [8]. The lattice parameters decrease linearly with increasing Hf contents, reflecting smaller ionic radius of hafnium (85 pm) than that of zirconium (86 pm) [11]. Since the dependence of the lattice parameters on Hf contents follows the Vegard's law,  $Zr_{1-x}Hf_xW_2O_8$  is considered to form a complete solid solution.

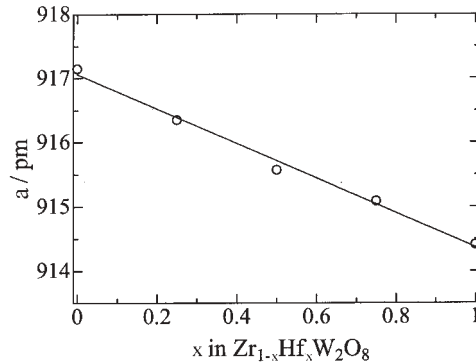


Fig. 2 Lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  at 121 K vs. Hf contents

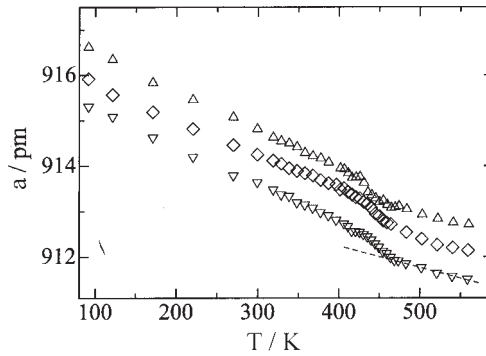
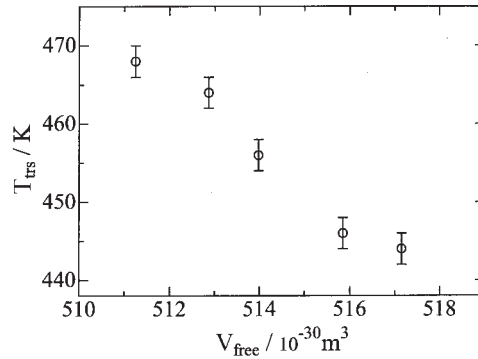
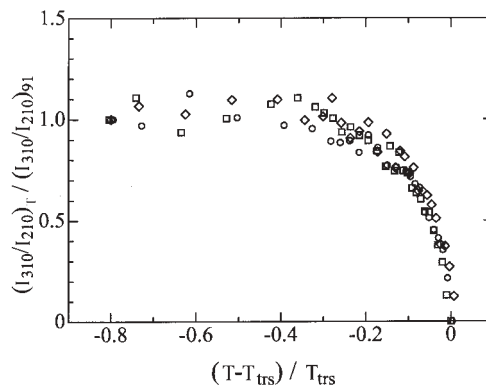


Fig. 3 Lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  as a function of temperature.  $\Delta$  –  $x=0.25$ ,  $\diamond$  –  $x=0.50$ ,  $\nabla$  –  $x=0.75$ . A dashed line for  $x=0.25$  is calculated from the fitting of lattice parameter vs. temperature above phase transition by a least square method

Figure 3 shows the lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) as a function of temperature. Anomalies in the lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) are seen for each sample in the temperature range from 400 to 500 K, similar to those for  $ZrW_2O_8$  and  $HfW_2O_8$  [8]. These anomalies are due to  $\alpha$ - $\beta$  phase transition. Transition temperatures are decided from disappearance of 310 diffraction peak in Fig. 1 and from the temperature where the lattice parameter curve of low temperature phase reaches the extrapolated line of the lattice parameters in high temperature phase. A typical extrapolation line of  $Zr_{0.25}Hf_{0.75}W_2O_8$  determined by a least square method is shown as a dashed line in Fig. 3. Phase transition temperatures ( $T_{trs}$ ) of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) were determined to be 446, 456 and 464  $\pm 2$  K, respectively. The increase of phase transition temperatures is considered to be due to the decrease of free space around  $WO_4$  unit on going from  $ZrW_2O_8$  to  $HfW_2O_8$ , because this structural phase transition is related to the orientation of the unshared



**Fig. 4** Phase transition temperatures of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.50$  and  $0.75$ ) vs. the calculated lattice free volumes ( $V_{\text{free}}$ ) in unit cell at 121 K.  $T_{\text{trs}}$  and lattice free volume of  $ZrW_2O_8$  and  $HfW_2O_8$  in our previous study [8] are also shown



**Fig. 5** Normalized intensities of  $(I_{310}/I_{210})_T / (I_{310}/I_{210})_{91}$  for  $Zr_{1-x}Hf_xW_2O_8$  as a function of  $(T - T_{\text{trs}}) / T_{\text{trs}}$ .  $\circ - x=0$ ,  $\diamond - x=0.50$ ,  $\square - x=1.0$

vertex of  $WO_4$  unit in the framework structure of  $ZrO_6$  and  $HfO_6$ . We define the lattice free volume ( $V_{\text{free}}$ ) as  $V_{\text{free}} = V - V_{\text{ion}}$ , where  $V$  is the unit cell volume and  $V_{\text{ion}}$  is the sum of the volumes for all ions occupying the unit cell. By using the lattice parameter in this study and the ionic radius in the literature [11], lattice free volume of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0-1.0$ ) in unit cell is calculated. Phase transition temperatures ( $T_{\text{trs}}$ ) of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) in this study, together with those of  $ZrW_2O_8$  and  $HfW_2O_8$  by our previous study [8] are plotted as a function of the calculated lattice free volume ( $V_{\text{free}}$ ) at 121 K. The correction of ionic radius at 121 K is not carried out for simplicity. The phase transition temperatures increase with decreasing lattice free volume as expected.

The 310 peak in Fig. 1 is considered to be one indicator of the observed parameters on order-disorder type phase transition, since the 310 diffraction peak disap-

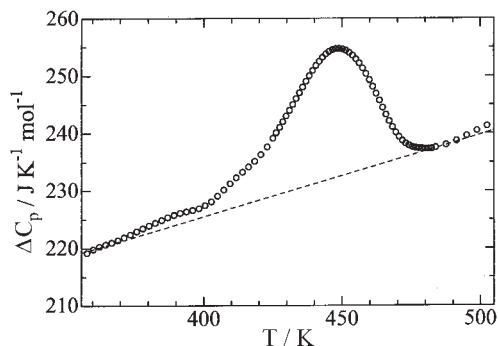


Fig. 6 Heat capacity of  $Zr_{0.5}Hf_{0.5}W_2O_8$  as a function of temperature

peared above  $\alpha$ - $\beta$  structural phase transition temperature, where  $P2_13$  at low temperature changes to  $Pa3$  at high temperature. The relative intensities of  $(I_{310}/I_{210})_T$  at the temperature  $T$  was calculated from XRD profiles, where  $I_{310}$  and  $I_{210}$  are intensities of 310 and 210 diffraction peaks, respectively. Figure 5 shows normalized intensity  $(I_{310}/I_{210})_T / (I_{310}/I_{210})_{91}$  as a function of  $(T-T_{trs})/T_{trs}$ , where  $(I_{310}/I_{210})_{91}$  is the relative intensity at 91 K. The normalized intensities of  $Zr_{0.5}Hf_{0.5}W_2O_8$  follow the same curve as those of  $ZrW_2O_8$  and  $HfW_2O_8$ . The normalized intensities are constant in the low temperature region and approach to zero at  $T_{trs}$ . These facts support that  $Zr_{0.5}Hf_{0.5}W_2O_8$  has the same phase transition mechanism as  $ZrW_2O_8$  and  $HfW_2O_8$ .

Figure 6 shows heat capacities of  $Zr_{0.5}Hf_{0.5}W_2O_8$  as a function of temperature. Anomaly in the heat capacity is seen at about 450 K. The temperature range of the anomaly in the heat capacity seems corresponding to that of the anomaly in the result of X-ray experiment as seen in Fig. 3. The baseline was determined by interpolating heat capacities in both higher- and lower-temperature ranges excluding the phase transition. The excess heat capacities of  $Zr_{0.5}Hf_{0.5}W_2O_8$  are obtained by subtracting the baseline and the results are shown in Fig. 7. The shape of the excess heat capacity for  $Zr_{0.5}Hf_{0.5}W_2O_8$  was similar to those of  $ZrW_2O_8$  and  $HfW_2O_8$  in our previous works [7, 8]. This  $\alpha$ - $\beta$  structural

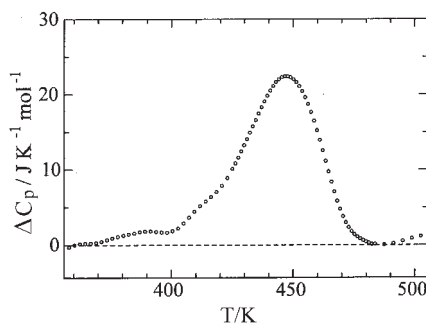
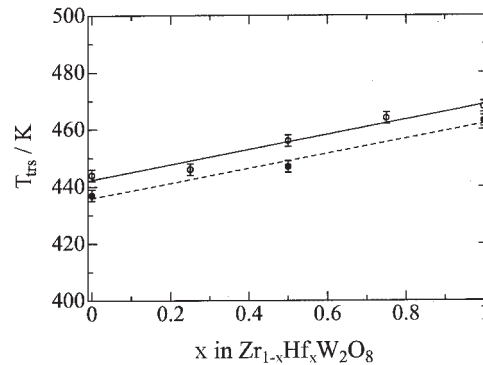


Fig. 7 Excess heat capacity of  $Zr_{0.5}Hf_{0.5}W_2O_8$  as a function of temperature



**Fig. 8** Phase transition temperatures of  $Zr_{1-x}Hf_xW_2O_8$  vs. Hf contents. Open and solid circles are determined by X-ray diffraction and calorimetric measurements, respectively

phase transition is regarded as  $\lambda$ -type, which is a general shape of second-order phase transition. In calorimetric measurement, transition temperature was decided from the peak in heat capacity to be 447 K, which is 9 K lower than that determined by X-ray diffractometry. The temperature difference is attributed to gas environment around the sample in ASC and XRD equipments. In ASC the sample in the calorimeter vessel is in some He gas to assist quick thermal equilibration. On the other hand, the XRD measurement is carried out under vacuum environment, where the sample shows poorer thermal conductivity due to larger gas thermal resistance among particles. This different thermal conductivity of sample between XRD and ASC may lead to the difference in the phase transition temperature. Figure 8 shows transition temperatures of  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0.25, 0.5$  and  $0.75$ ) determined by X-ray diffractometry and that of  $Zr_{0.5}Hf_{0.5}W_2O_8$  by heat capacity measurement, together with those of  $ZrW_2O_8$  and  $HfW_2O_8$  by our previous studies [7, 8]. Transition temperatures obtained from both measurements increase with increasing Hf contents.

Transition entropies and enthalpies were estimated from numerical integration of the excess heat capacity. The transition enthalpy and entropy of  $Zr_{0.5}Hf_{0.5}W_2O_8$  are decided to be  $924 \pm 10 \text{ J mol}^{-1}$  and  $2.1 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. The transition entropy of  $Zr_{0.5}Hf_{0.5}W_2O_8$  is consistent with that of  $ZrW_2O_8$  and  $HfW_2O_8$  ( $2.1 \text{ J mol}^{-1} \text{ K}^{-1}$ ) [7, 8]. The consistent entropy supports that  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0-1.0$ ) has the same order-disorder type phase transition mechanism, which two  $WO_4$  tetrahedra on [111] diagonal in the unit cell have only two conformations in a concerted manner.

## Conclusions

Effects of Hf contents on lattice parameter and phase transition of  $Zr_{1-x}Hf_xW_2O_8$  solid solutions were studied by X-ray diffraction and calorimetric measurements. The lattice parameters of  $Zr_{1-x}Hf_xW_2O_8$  decreased linearly with increasing Hf contents, reflecting smaller ionic radius of Hf than that of Zr. Transition temperatures due to  $\alpha$ - $\beta$  structural

phase transition increased with increasing Hf contents, reflecting the decrease of lattice free volume which has difficulty in the orientation of unshared vertex of two  $WO_4$  tetrahedra. Transition entropy and normalized 310 peak intensity of  $Zr_{0.5}Hf_{0.5}W_2O_8$  determined by XRD as a function of  $(T-T_{trs})/T_{trs}$  was consistent with those of  $ZrW_2O_8$  and  $HfW_2O_8$ . These facts support that  $Zr_{1-x}Hf_xW_2O_8$  ( $x=0-1.0$ ) has the same phase transition mechanism.

## References

- 1 T. A. Mary, J. S. O. Evans, T. Vogt and A. W. Sleight, *Science*, 272 (1996) 90.
- 2 J. S. O. Evans, T. A. Mary, T. Vogt, M. A. Subramanian and A. W. Sleight, *Chem. Mater.*, 8 (1996) 2809.
- 3 J. S. O. Evans, W. I. F. David and A. W. Sleight, *Acta Crystallogr., Sect. B: Struct. Sci.*, 55 (1999) 333.
- 4 A. P. Ramirez and G. R. Kowach, *Phys. Rev. Lett.*, 80 (1998) 4903.
- 5 G. Ernst, C. Broholm, G. R. Kowach and A. P. Ramirez, *Nature*, 396 (1998) 147.
- 6 A. W. Sleight, T. A. Mary and J. S. O. Evans, U.S. Patent number 5514360, 1995.
- 7 Y. Yamamura, N. Nakajima and T. Tsuji, *Solid State Commun.*, 114 (2000) 453.
- 8 Y. Yamamura, N. Nakajima and T. Tsuji, *Phys. Rev. B*, 64 (2001) 184109.
- 9 D. G. Archer, *J. Phys. Chem. Ref. Data*, 22 (1993) 1441.
- 10 J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.*, 57 (1945) 160.
- 11 R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.*, A32 (1976) 751.