Phase Transition of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ Solid Solutions Having Negative Thermal Expansion

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The phase transition of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ ($x = 0–1$) solid solutions substituted for $\text{Zr}^{IV}$ sites was investigated using X-ray diffraction, TMA and DSC methods. X-ray diffraction experiments revealed that all compositions of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ ($x = 0–1$) were of a single phase having a cubic structure. Lattice parameters of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ ($x = 0–1$) samples also underwent two successive phase transitions between 330 and 390 K. Two transition temperatures and phase transition enthalpies of $\text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_7$ ($x = 0–1$) samples decreased with the increase of $x$ content, reflecting the decrease of superlattice structure. The sum of transition entropy for successive two phase transitions increased with increasing the normalized relative intensity of the superlattice line at room temperature.

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1. Introduction

There are many interesting potential applications of compounds which present a low or negative thermal expansion, such as $\text{ZrV}_2\text{O}_5$, $\text{ZrW}_2\text{O}_7$, or $\text{Y}_2\text{W}_2\text{O}_7$. These compounds are of great interest, since they can be added to a positive thermal expansion material in order to create composite materials which exhibit a low or zero thermal expansion.

Figure 1 shows the ideal cubic crystal structure of $\text{ZrV}_2\text{O}_5$, having a space group $\text{P}6_3$. The ideal cubic structure of $\text{ZrV}_2\text{O}_5$ can be considered as related to the NaCl structure, with the $\text{ZrO}_2$ octahedron centered at the ideal Na site and the bridging oxygen of the $\text{V}_2\text{O}_7$ group ($\text{O}_3\text{V}-\text{O}-\text{VO}_3$) at the Cl site.

Withers et al. reported from TMA measurement that $\text{ZrV}_2\text{O}_5$ showed two phase transitions at around 350 and 375 K, and a negative isotropic thermal expansion was observed over a wide temperature range from 375 to 1050 K. Negative thermal expansion is interpreted to be caused by transverse thermal vibration of the central oxygen atom in perpendicular to the bonding direction of $\text{O}_3\text{V}-\text{O}-\text{VO}_3$ with increasing temperature. DSC measurement of $\text{ZrV}_2\text{O}_5$ by Korthuis et al. also showed two phase transitions at around 350 and 375 K, and these phase transitions were reported to be of the first order phase transition due to thermal hysteresis. Below 350 K a $\text{P}3 \times 3 \times 3$ superstructure was observed, and the superstructure contains 108 octahedra and 216 tetrahedra in each unit cell. There is no clear change in the space group in 350 K-phase transition, and a superstructure disappears in 375 K or more, though $\text{ZrV}_2\text{O}_5$ is a $3 \times 3 \times 3$ superstructure at room temperature. An incommensurate structure was seen between 350 and 375 K.

$\text{HfV}_2\text{O}_5$ was first studied in 1976 by Baran who noted that its room temperature powder diffraction profile could be indexed with a cubic cell of about 876 pm edge, and had the same crystal structure as $\text{ZrV}_2\text{O}_5$. Turquat et al. reported from TMA and DSC measurements that $\text{HfV}_2\text{O}_5$ showed two phase transitions at around $T_1 = 340 \text{ K}$ and $T_2 = 369 \text{ K}$, and negative thermal expansion above 370 K, similarly to those of $\text{ZrV}_2\text{O}_5$. Two transition temperatures depend on the cooling rate, but independent of the heating rate. They considered that the phase transition at low temperature is the first order, whereas phase transition at high temperature is the second order due to thermal hysteresis. Crystal structure and thermal expansion data are available for $\text{ZrV}_2\text{O}_5$ substituted for V sites by P ions, but for the substitution of Zr site, any report of crystal structure and thermodynamic data of $\text{ZrV}_2\text{O}_5$ has not been reported.
been reported yet.

It is well known that zirconium and hafnium ions resemble each other in chemical properties. 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. In this study, Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) solid solutions were synthesized by a solid-sate-reaction method, and Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) prepared were investigated using X-ray diffraction, TMA and DSC methods. Effect of Hf substituted content on lattice parameter, thermal expansion coefficient and phase transition such as transition temperature, transition enthalpy and entropy of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) solid solutions were studied and discussed.

2. Experimental

All samples of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) were synthesized from the starting materials of ZrO$_2$ (Nacalai Tesque, Inc., 99.5%), HfO$_2$ (Kojundo Chemical Lab., 99%) and NH$_4$VO$_3$ (Kojundo Chemical Lab., 99%) by a solid-state reaction method. Starting materials with appropriate ratios were first mixed for 15 min in n-hexane and for 2 h in air in an agate mortar. The mixture obtained was then placed on the platinum foil in an alumina boat, heated at 923 K in air for 24 h and cooled down to room temperature. The sample was reground for 2 h to get homogeneous solid solution, pressed isostatically at 40 MPa to make a pellet of 6 mm in a diameter and heated again at 1023 K in air for 24 h. These processes were repeated two times to make sure that the reaction was complete.

All samples prepared were characterized by a powder X-ray diffraction (XRD) method using Cu Kα radiation with 40 kV–100 mA (or 200 mA) (RINT 2500 V by Rigaku Co., Ltd.). The XRD data were collected in air by a step scanning method in the 2θ range from 5 to 120° with a step width of 0.01° (or 0.05°) and a counting time of 0.5 s (or 10 s). Linear thermal expansions of prepared samples were measured in air at temperatures from 300 to 873 K at the heating rate of 2 K/min by means of Thermo Mechanical Analysis (TMA8310 by Rigaku Co., Ltd.) method. Thermodynamic properties of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) samples were also measured at temperatures from 113 to 473 K in He atmosphere at the heating and cooling rate of 10 K/min by a power-compensation type Differential Scanning Calorimeter (DSC, Pyris 1 by Perkin Elmer Co., Ltd.).

3. Results and discussion

Room temperature X-ray diffraction profiles of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) samples are shown in Fig. 2, where X-ray diffraction profiles are similar each other. All samples of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) were characterized to be of a single phase having the same cubic crystal structure as ZrV$_2$O$_7$. The diffraction peaks in the X-ray profiles of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) were assigned by referring to the previous work on ZrV$_2$O$_7$. Lattice parameter of the sample was determined using about 20 diffraction peaks between 35 and 80° by a least-square method after correcting 2θ with Nelson–Riley’s method. The lattice parameters of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) at room temperature as a function of x content are plotted in Fig. 3, where lattice parameter of ZrV$_2$O$_7$ by Evans et al. and that of HfV$_2$O$_7$ by Turquat et al. are also shown. Lattice parameters of the end members in this study are in good agreement with those reported by the previous works. The lattice parameters of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) decrease linearly with increasing the substituted x content, reflecting the smaller ionic radius of the Hf(IV) ion (86 pm) than that of the Zr(IV) ion (86 pm) in the octahedral site. Since the compositional dependence of the lattice parameters of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$–$1$) follows the Vegard’s law, the ZrV$_2$O$_7$–HfV$_2$O$_7$ system is considered to form a complete solid solution.

Figure 4 shows the temperature dependence of the relative linear thermal expansion, $(L_T-L_{298})/L_{298} \times 100(\%)$ of Zr$_{1-x}$Hf$_x$V$_2$O$_7$ ($x=0$, 0.5, 1) solid solutions, where $L_T$ and $L_{298}$ are a sample length at $T$ and 298 K, respectively. Two abrupt jumps in the relative linear thermal expansion of three samples are seen at around $T_1=350$ K and $T_2=375$ K, and decreased with increasing the substituted x content. Negative thermal expansion for three samples is also seen above around 375 K. Larger (or smaller) thermal hysteresis at around transition temperature of $T_1$ (or $T_2$) was observed for heating and cooling processes. From an abrupt jump in the thermal expansion and thermal hysteresis for heating and cooling processes, it is concluded that both phase transitions of $T_1$ and $T_2$ are the first order phase transition. A linear thermal expansion coefficient $\alpha=(1/L_{298})(dL/\Delta T)$ at each temperature is calculated by a least square method from 200 point data of $dL/L_{298}$ in the temperature range from 298 K.
interval of 7 K in Fig. 4, and the results are shown in Fig. 5. Transition temperature of \( T_1 \) or \( T_2 \) was determined from a peak temperature of \( \alpha \) value. Transition temperatures of \( T_1 \) and \( T_2 \) are seen at around 350 and 375 K, respectively, and decrease with increasing \( x \) content. Negative thermal expansion coefficient was determined to be \(-7.2 \times 10^{-6} \, \text{K}^{-1}\), independent of \( x \) content. Negative thermal expansion is interpreted to be caused by transverse thermal vibration of the central oxygen atom in perpendicular to the bonding direction of \( \text{O}_2\text{V–O–VO}_3 \) with increasing temperature.\(^{29}\) It is thus considered that the substitution of hafnium for zirconium site does not influence the transverse thermal vibration of \( \text{O}_2\text{V–O–VO}_3 \), but is effective to the transition temperature.

DSC results of \( \text{Zr}_{0.25}\text{Hf}_{0.75}\text{V}_2\text{O}_5 \) for the heating and cooling rate of 10 K/min are shown in Fig. 6. Transition temperature of \( T_1 \) or \( T_2 \) was determined from a peak temperature. A transition temperature at around \( T_1 = 343 \, \text{K} \) of \( \text{Zr}_{0.25}\text{Hf}_{0.75}\text{V}_2\text{O}_5 \) at heating process is higher than that at around \( T_1 = 333 \, \text{K} \) at cooling process, and shows a large thermal hysteresis at around \( T_1 \). Small thermal hysteresis at around \( T_2 = 371 \, \text{K} \) is also seen for heating and cooling processes. Similar thermal hystereses at \( T_1 \) and \( T_2 \) were observed for all other Hf content. From an abrupt positive jump in thermal expansion in TMA in Fig. 4 and thermal hysteresis for cooling and heating processes in TMA and DSC data, it is thus concluded that both phase transitions at \( T_1 \) and \( T_2 \) are the first order phase transition. Figure 7 shows DSC curves of \( \text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_5 \) (\( x = 0-1 \)) at the heating rate of 10 K/min. DSC results clearly show that all of the \( \text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_5 \) (\( x = 0-1 \)) samples undergo two successive phase transitions between room temperature and 450 K as expected from TMA measurement. Both transition temperatures of \( T_1 \) and \( T_2 \) in DSC decrease with the increase in the substituted \( x \) content, consistent with the results by TMA in Fig. 5. The first peak at \( T_1 \) in DSC may be a phase transition from a \( 3 \times 3 \times 3 \) superstructure to an incommensurate structure as proposed by Withers et al.\(^{31}\) The second peak at \( T_2 \) in DSC curve may correspond to phase transition from an incommensurate structure to the ideal crystal structure with disappearance of the superlattice as discussed by Withers et al.\(^{12}\)

Transition temperatures, \( T_1 \) and \( T_2 \) for \( \text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_5 \) (\( x = 0-1 \)) solid solutions determined from peak temperatures in TMA (see Fig. 5) and DSC (see Fig. 7) are plotted as a function of the substituted \( x \) content in Fig. 8, where transition temperatures reported by Korthus et al. are also shown.\(^{35}\) Transition temperatures of \( T_1 \) and \( T_2 \) of \( \text{Zr}_x\text{V}_2\text{O}_5 \) in this study are in good agreement with those of the previous study. Phase transition temperatures of \( \text{Zr}_{1-x}\text{Hf}_x\text{V}_2\text{O}_5 \) (\( x = 0-1 \)) solid solu-
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![Graph](image1)

**Fig. 8.** Phase transition temperatures (T_1, T_2) of Zr_{1−x}Hf_{x}V_2O_7 (x=0-1) determined from peak temperatures in TMA (see Fig. 5) and DSC (see Fig. 7) as a function of x content.

![Graph](image2)

**Fig. 9.** Phase transition enthalpy Δ_h of Zr_{1−x}Hf_{x}V_2O_7 (x=0-1) as a function of x content.

![Graph](image3)

**Fig. 10.** Phase transition entropies Δ_s of Zr_{1−x}Hf_{x}V_2O_7 (x=0-1) as a function of x content.

![Graph](image4)

**Fig. 11.** XRD profile of ZrV_2O_7 at room temperature.

Phases are observed in Zr_{1−x}Hf_{x}V_2O_7 with increasing the substituted x content. Transition temperature obtained by TMA method is higher than that obtained by DSC measurement, because a cylindrical pellet used for TMA is needed longer time to reach a steady state than powder sample used for DSC.

In order to calculate the transition enthalpy, we need to estimate the base line. The base line was determined by interpolating DSC data in both higher- and lower-temperature ranges smoothly excluding the phase transition. Phase transition enthalpy, Δ_h, is calculated from an integrated area, S, by using the equation, Δ_h = S / (sample weight / (molecular weight)). Phase transition enthalpies of Zr_{1−x}Hf_{x}V_2O_7 (x = 0-1) at T_1 and T_2 are plotted as a function of x content in Fig. 9, where both transition enthalpies at T_1 and T_2 decrease with increasing x content, reflecting the decrease of transition temperature.

The first order structural phase transition temperature, the following relation is hold:

\[ Δ_s = \frac{Δ_h}{T_{trs}} \]  

where Δ_s is a transition entropy. Either transition entropy of Δ_s at T_1 or Δ_s at T_2 is calculated from the Eq. (1) by using phase transition enthalpy in Fig. 9 and transition temperature in Fig. 8. Phase transition enthalpies of Zr_{1−x}Hf_{x}V_2O_7 (x = 0-1) at T_1 and T_2 are plotted as a function of x content in Fig. 10, where phase transition entropies decrease with increasing x content.

Let us consider the relation between thermodynamic properties and crystal structure. Figure 11 shows an XRD profile of ZrV_2O_7 sample at room temperature. The 911 superlattice peak in the figure is considered to be one indicator of the observed parameters on the structural phase transition, since the 911 superlattice diffraction peak disappeared above the second phase transition temperature. The relative intensity of \( I_{911} / I_{660} \) for Zr_{1−x}Hf_{x}V_2O_7 was calculated from XRD profile in Fig. 11, where \( I_{911} \) and \( I_{660} \) are intensities of the 911 superlattice and 660 main-lattice diffraction peaks, respectively. The normalized relative intensity, \( \xi \), is calculated as follows:

\[ \xi = \sqrt{\frac{I_{911} / I_{660}}{I_{911} / I_{660}}} \]  

The \( \xi \) values calculated from Eq. (2) are shown as a function of the substituted x content in Fig. 12. The \( \xi \) values decrease with increasing x content, indicating the decrease of the superlattice peak at high x content.

The relation between transition temperature and normalized relative intensity \( \xi \) is shown in Fig. 13, where both transition temperatures of T_1 and T_2 increase with increasing \( \xi \) value. Below 350 K a 3×3×3 superstructure is observed, there is no clear change in the space group in 350 K-phase transition, and a superstructure disappears in 375 K or more. In other word,
Increasing the Fig. 14 and the results are shown in Fig. 10 for the successive two phase transitions of sized by a solid-state-reaction method. Linear compositional HfV peak.

A 3 × 3 × 3 superstructure of ZrV₂O₇ was observed below 350 K and disappears above 375 K. The transition entropy is related to the disappearance of superlattice peak. The sum of transition entropy for successive two phase transitions increased with increasing the normalized relative intensity because a superlattice peak partially disappears at T₁ and completely disappears at T₂. From Figs. 11 and 12, a strong superlattice peak of ZrV₂O₇ corresponding to high ζ value requires high transition temperature, whereas a weak superlattice peak of HfV₂O₇ shows low transition temperature.

A 3 × 3 × 3 superstructure of ZrV₂O₇ was observed below 350 K and disappears above 375 K. Thus the sum of transition entropy is related to the disappearance of superlattice peak. The sum of transition entropy, ΣΔₓS = ΔₓS(1) + ΔₓS(2) was calculated from Fig. 10 for the successive two phase transitions of T₁ and T₂, and the results are shown in Fig. 14 as a function of the normalized relative intensity ζ value. The sum of transition entropy, ΣΔₓS, of Zr₁−ₓHfₓV₂O₇ (x = 0–1) increases with increasing the ζ value, because a superlattice peak of ZrV₂O₇ is stronger than that of HfV₂O₇ as seen in Fig. 12.

4. Conclusions

Zr₁−ₓHfₓV₂O₇ (x = 0–1) solid solutions substituted for Zr (IV) site were investigated using X-ray diffraction, TMA and DSC methods, and the following conclusions are derived.

1) Zr₁−ₓHfₓV₂O₇ (x = 0–1) solid solutions substituted for Zr (IV) site by the same tetravalent Hf (IV) ions were synthesized by a solid-state-reaction method. Linear compositional dependence of lattice parameter obtained by X-ray diffraction experiment revealed that this system formed a complete solid solution. The lattice parameters of Zr₁−ₓHfₓV₂O₇ (x = 0–1) decreased with increasing x content, reflecting the smaller ionic radius of the Hf ion than that of the Zr ion.

2) Two successive structural phase transitions of Zr₁−ₓHfₓV₂O₇ (x = 0–1) solid solutions were observed at around 350 and 375 K by DSC and TMA measurements, respectively. Both transition temperatures were the first order phase transition and decreased with increasing x content, reflecting the decrease of the superlattice structure at high x content.

3) Zr₁−ₓHfₓV₂O₇ (x = 0.25–0.75) solid solutions changed from a positive thermal expansion to a negative one at around 380 K by TMA method, and a linear negative thermal expansion coefficient of all samples was about −7.2 × 10⁻⁴ K⁻¹, independent of x content.

4) Transition enthalpy decreased with increasing x content, indicating low transition temperature at high x content.

5) The sum of the transition entropy for successive two phase transitions increased with increasing the normalized relative intensity of the superlattice line at room temperature.

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