Thermal Analysis of Phase Transition in Negative-Thermal-Expansion Oxide, ZrW_2O_8

—Detection of Trace Amount of H_2O and λ -Type Transition—

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熱収縮性酸化物 ZrW_2O_8 の構造相転移の熱分析

—微量 H_2O 及び λ 転移の検出—

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Differential scanning calorimetry (DSC) curves of negative-thermal-expansion oxide, ZrW_2O_8 , were obtained under dry N_2 atmosphere. An endothermic peak and base-line shift were observed at 124 and 169°C, respectively, upon heating measurements of as-prepared ZrW_2O_8 . Upon successive cooling and heating measurements, the base-line shift at 169°C was reproduced, however, the peak at 124°C disappeared in both curves. The base-line shift at 169°C corresponded to the variation of the thermal expansion coefficient due to a structural phase transition from the acentric cubic phase with the space group of $P2_13$ (No. 198) to the centric phase with the space group of $Pa\bar{3}$ (No. 205). Thermogravimetry (TG) and thermogravimetry differential thermal analysis mass spectroscopy (TG-DTA-MS) simultaneous measurement revealed that the origin of the endothermic peak at 124°C was the secession of H_2O involved with the ZrW_2O_8 specimen, whose amount was less than 1.6 mol%. It was clarified that the trace amount of H_2O negligibly affected the thermal expansion behavior of ZrW_2O_8 and that the variation of the thermal expansion coefficient around 164°C could be attributed to the λ -type transition.

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1. Introduction

The negative thermal expansion of ZrW_2O_8 has been confirmed by several researchers employing dilatometry, neutron diffraction and X-ray diffraction.¹⁾⁻⁵⁾ All of them detected discrete variation of the thermal expansion coefficient around 160°C due to structural phase transition. Evans and coworkers carried out Rietveld refinement of the neutron diffraction patterns of ZrW_2O_8 at various temperatures.^{3),5)} They proposed that the crystal structure of the phase below ~160°C, called “ α -phase,” was cubic with the acentric space group of $P2_13$ (No. 193), including the ordered orientation of WO_4 tetrahedra by [111] direction. It was also proposed that the orientation of WO_4 tetrahedra was distorted above ~160°C, resulting in the phase transition to the so-called “ β -phase” with the centric space group of $Pa\bar{3}$ (No. 205). Although the thermodynamic character of the phase transition was not clarified, they regarded the phase transition as a second-order one since the transition was an order-disorder type transition. Yamamura et al. carried out adiabatic calorimetry and concluded that the phase transition at 163°C was of the second order.⁶⁾ Differential scanning calorimetry (DSC) measurement has advantages such as the much lower sample amount required for measurement and a simpler system than adiabatic calorimetry. However, it has been reported that the phase transition cannot be detected with DSC.^{3),4)}

Recently, we have succeeded in observing for the first time the second-order phase transition of ZrW_2O_8 by using the power-compensated DSC at 164°C.⁷⁾ In the DSC curve, the endothermic peak was observed at ~123°C, in addition to the base-line shift at 164°C corresponding to the second-order phase transition. Since three phases with different

thermal expansion coefficients were apparently observed in the temperature dependence of lattice constants measured with X-ray diffraction, it was suspected that the endothermic peak originated from a structural phase transition. However, X-ray diffraction patterns showed little difference between 120 and 130°C. In this study, power-compensated DSC and thermogravimetry (TG) measurements under dry N_2 or dry Ar atmosphere and thermogravimetry differential thermal analysis mass spectroscopy (TG-DTA-MS) simultaneous measurement were carried out to clarify the origin of the endothermic peak observed at ~124°C. Since it was revealed that the peak originated from the trace amount of H_2O involved in the ZrW_2O_8 specimen, its effect on thermal expansion behavior was investigated by dilatometry. The analysis of the phase transition by using a dilatometer and employing H_2O -free ZrW_2O_8 as a sample was also carried out.

2. Experimental

A ZrW_2O_8 ceramic specimen was prepared by the solid-state reaction method. Powdery ZrO_2 (99.9%) and WO_3 (99.9%) were mixed with the correct stoichiometric proportion in ethanol. The mixture was pressed into a pellet with ~20 mm diameter and ~5 mm thickness. The pellet was enveloped with platinum foil to prevent vaporization of WO_3 during the heat treatment.⁸⁾ The specimen was heated at 1200°C for 17 h in open air, followed by quenching to room temperature. The obtained specimen was confirmed to be single-phase cubic ZrW_2O_8 with a lattice constant of 0.9155 nm by using powder X-ray diffraction (Rigaku Co., Ltd.: RINT-2500), which agreed well with the previously reported values.^{2),3)} The density of the sintered pellet was ~70%

of the ideal one.

Power-compensated DSC was carried out by using a Perkin-Elmer Pyris-1 system. The powdery ZrW_2O_8 sample (10.915 mg) was sealed in an aluminum cell to improve thermal conduction. It was not expected that the seal would be perfectly airtight. The sample was heated with a rate of temperature increase of $10^\circ\text{C}/\text{min}$ from room temperature to 200°C , followed by successive cooling to room temperature with a rate of temperature decrease of $10^\circ\text{C}/\text{min}$. Again, the sample was heated to 200°C at $10^\circ\text{C}/\text{min}$ heating rate. All these procedures were performed in dry N_2 atmosphere. The heat capacity of the specimen and the absorption and/or generation of heat during the procedures were measured directly. An empty aluminum pan was employed as a reference.

In order to distinguish whether a gas component was generated from a specimen or not, TG and TG-DTA-MS simultaneous measurements were performed using a Rigaku TG8120 and a Rigaku Thermomass, respectively. TG measurement was carried out under flowing dry Ar at 150 ml/min. The ZrW_2O_8 powder (58.9 mg) was loaded in a Pt pan and the weight variation with temperature was measured with a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature to 200°C . The measurement with decrease of temperature from 200 to 50°C was then successively performed with a cooling rate of $10^\circ\text{C}/\text{min}$. The TG-DTA-MS simultaneous measurement was carried out under He atmosphere with a flow rate of 200 ml/min. 67.62 mg of the specimen, loaded in a Pt pan, was heated at the rate of $20^\circ\text{C}/\text{min}$ and TG-DTA was measured. An empty Pt pan was used as a reference. The gas component was analyzed using a mass spectrometer equipped at the downstream of the TG-DTA apparatus.

Dilatometry was carried out by using a Rigaku TMA8310 to estimate the thermal expansion behavior of ZrW_2O_8 ceramics. The rectangular specimen of $4.80\text{ mm} \times 4.65\text{ mm} \times 15.00\text{ mm}$ size cut from the pellet and the Al_2O_3 rod with 15.00 mm length were employed as the sample and reference, respectively. The thermal expansion behavior in the temperature range from 25 to 250°C was recorded in dry Ar, followed by successive cooling to 50°C with a $10^\circ\text{C}/\text{min}$ rate of heating and cooling. Again, the thermal expansion behavior in the temperature range was successively measured with a heating rate of $10^\circ\text{C}/\text{min}$.

3. Results and discussion

3.1 DSC measurement of ZrW_2O_8 under dry N_2 atmosphere

Figure 1 shows the DSC curves of ZrW_2O_8 under N_2 atmosphere. The DSC curve for the heating process of as-prepared ZrW_2O_8 was represented by a solid curve. The endothermic peak and base-line shift were observed at 124 and 169°C , respectively, showing agreement with the previously reported DSC curve measured in air.⁷⁾ The base-line shift at 169°C was reproduced in successive cooling and heating measurements as represented by dashed and chain curves in Fig. 1, respectively, showing agreement with the reversible structural phase transition observed by several researchers.^{2),3),5)-7)} However, the endothermic peak disappeared in successive cooling and heating measurements, suggesting that the peak at 124°C originated from the removal of some components from as-prepared ZrW_2O_8 to gas phase.

3.2 TG measurement of ZrW_2O_8 under Ar atmosphere

Figure 2 shows the TG curve of ZrW_2O_8 under dry Ar atmosphere. In the heating process of as-prepared ZrW_2O_8 , weight decrease was observed in the temperature range from room temperature to $\sim 130^\circ\text{C}$. Almost a constant weight was observed above $\sim 130^\circ\text{C}$ during the heating measurement. During the cooling process, weight increase was not observed and the weight at room temperature of the as-prepared specimen was not reproduced. It was suggested that some components were irreversibly removed from the specimen with the increase of temperature in dry Ar atmosphere, showing agreement with the results of DSC measurement.

3.3 TG-DTA-MS simultaneous measurement of as-prepared ZrW_2O_8

In order to identify the component removed from as-prepared ZrW_2O_8 at $\sim 124^\circ\text{C}$, TG-DTA-MS simultaneous measurement was carried out and the result is shown in Fig. 3. In the DTA curve, the endothermic peak and base-line shift were observed at 124 and 167°C , respectively, showing agreement with the results of DSC measurement of as-prepared ZrW_2O_8 shown in Fig. 1. Weight decrease was observed in the TG curve above $\sim 110^\circ\text{C}$. Simultaneous measurement by mass spectroscopy revealed that the molecular weight of the component removed from as-prepared ZrW_2O_8 above $\sim 110^\circ\text{C}$ was 18, indicating that the endothermic DTA peak at 124°C can be attributed to the secession of H_2O involved with the as-prepared ZrW_2O_8 .

Figure 3 indicated that $\sim 0.055\%$ of the as-pre-

Fig. 1

Fig. 2

Fig. 3

Fig. 1. DSC curves of ZrW_2O_8 under dry N_2 atmosphere. Solid curve, heating procedure of as-prepared ZrW_2O_8 ; dashed curve, cooling procedure; chain curve, successive heating procedure. Heating and cooling rate is $10^\circ\text{C}/\text{min}$.

Fig. 2. TG curves of as-prepared ZrW_2O_8 in dry Ar atmosphere. Solid curve, heating procedure; and dashed curve, cooling procedure. Heating and cooling rate is $10^\circ\text{C}/\text{min}$.

Fig. 3. TG-DTA-MS simultaneous measurement of as-prepared ZrW_2O_8 under He flow. Rate of temperature increase is $20^\circ\text{C}/\text{min}$.

pared specimen was H_2O . The molar ratio of $\text{H}_2\text{O}/\text{ZrW}_2\text{O}_8$ was calculated to be 0.016. It cannot be definitely confirmed that the H_2O was involved in ZrW_2O_8 crystal or adsorbed on the surface of the specimen by this study alone. However, Duan et al. reported the preparation of $\text{ZrW}_2\text{O}_8 \cdot x\text{H}_2\text{O}$ ($0.5 \leq x \leq 1.0$) by heat treatment of ZrW_2O_8 at 180°C under a humid atmosphere.⁹ They observed the decrease of lattice constants with the increase of H_2O content, x , and proposed the structural model in which ZrW_2O_8 involves the H_2O molecule in the crystal. Therefore, it is suspected that H_2O as identified in this study was involved in the crystal during the preparation process under open air and that its content in the as-prepared specimen was so small that the lattice constant was scarcely affected.

3.4 Dilatometry of ZrW_2O_8 ceramic specimen

Figure 4 shows the dependence of thermal expansion and thermal expansion coefficient on temperature, as obtained with a dilatometer. The thermal expansion coefficient, α (T), was calculated by using the following formula.

$$\alpha(T) = 1/L(T) (\partial L(T)/\partial T)$$

Here, T and $L(T)$ indicate the temperature and length of the specimen at temperature, T . The thermal expansion behavior of as-prepared ZrW_2O_8 during the heating process was represented by a solid curve. An almost constant negative-thermal-expansion coefficient ($-1.0 \times 10^{-5} \text{ K}^{-1}$) was observed below $\sim 110^\circ\text{C}$. The thermal expansion coefficient markedly decreased with the increase of temperature in the temperature range from 110 to 165°C . Above 165°C , the thermal expansion coefficient increased and showed an almost constant value of approximately $-5.6 \times 10^{-6} \text{ K}^{-1}$ above $\sim 195^\circ\text{C}$. Since this behavior apparently showed agreement with the endothermic peak and base-line shift observed in the DSC curve of as-prepared ZrW_2O_8 , we concluded that there were three phases in ZrW_2O_8 and that the temperature regions in which α -phase, γ -one and β -one were stable, were below $\sim 124^\circ\text{C}$, 124 – 169°C and above $\sim 169^\circ\text{C}$, respectively, in the preceding study.⁷ However,

dilatometry using the specimen that did not contain H_2O was required in order to analyze the thermal expansion behavior of ZrW_2O_8 since it was clarified that the endothermic DSC peak was due to H_2O vapor secession from the ZrW_2O_8 specimen and that the phase transition was observed only at $\sim 169^\circ\text{C}$ in the DSC curve.

Figure 4 shows the thermal expansion behavior of ZrW_2O_8 during successive cooling and heating processes as depicted by open squares and closed diamonds, respectively. The specimen in these procedures contained no H_2O , as Fig. 2 shows. There was scarcely any difference observed among the solid curve, open squares and closed diamonds, indicating that the trace of H_2O negligibly affected the thermal expansion behavior. The peak was observed in the temperature dependence of thermal expansion coefficient at 164°C , which agreed with the phase transition temperature observed with DSC. The peak shape showed a resemblance to one observed in the temperature dependence of excess heat capacity, ΔC_p , reported by Yamamura et al.⁶ From the relationship between ΔC_p vs. T , they concluded that the phase transition at $\sim 164^\circ\text{C}$ was second order, i.e., a λ -type transition. Since the thermal expansion coefficient is the second derivative of Gibbs free energy as heat capacity, it is reasonable that a λ -type peak shape was observed in the temperature dependence of thermal expansion coefficient at the transition temperature.

4. Conclusions

The endothermic peak at $\sim 124^\circ\text{C}$ observed in the DSC measurement of as-prepared ZrW_2O_8 was identified to be the secession of H_2O from the specimen by TG, DSC measurements under dry N_2 or dry Ar atmosphere and TG-DTA-MS simultaneous measurement. It was suspected that the H_2O was involved in the ZrW_2O_8 crystal. The molecular formula of the as-prepared specimen employed in this study was expressed as $\text{ZrW}_2\text{O}_8 \cdot \sim 0.016\text{H}_2\text{O}$. By using the H_2O -free specimen, it was established that the phase transition at $\sim 164^\circ\text{C}$ was of the second order, i.e., it was a λ -type transition.

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References

- 1) Martinek, C. and Hummel, F. A., *J. Am. Ceram. Soc.*, **51**, 227–28 (1968).
- 2) Mary, T. A., Evans, J. S. O., Vogt, T. and Sleight, A. W., *Science*, **272**, 90–92 (1996).
- 3) Evans, J. S. O., Mary, T. A., Vogt, T., Subramanian, M. A. and Sleight, A. W., *Chem. Mater.*, **8**, 2809–23 (1996).
- 4) Holzer, H. and Dunand, D. C., *J. Mater. Res.*, **14**, 780–89 (1999).
- 5) Evans, J. S. O., David, W. I. F. and Sleight, A. W., *Acta Cryst. B*, **55**, 333–40 (1999).
- 6) Yamamura, Y., Nakajima, N. and Tsuji, T., *Solid State Commun.*, **114**, 453–55 (2000).
- 7) Hashimoto, T., Katsube, T. and Morito, Y., *Solid State Commun.*, **116**, 129–32 (2000).
- 8) Hashimoto, T., Waki, T. and Morito, Y., *Proc. of the Institute of Natural Sciences, Nihon Univ.*, **36**, 121–26 (2001).
- 9) Duan, N., Kameswari, U. and Sleight, A. W., *J. Am. Chem. Soc.*, **121**, 10432–33 (1999).

Fig. 4. Thermal expansion and thermal expansion coefficient, α , of ZrW_2O_8 ceramic specimen measured with dilatometer: solid curve, heating procedure of as-prepared ZrW_2O_8 ; $\square$ cooling procedure; and $\blacklozenge$ successive heating procedure. A λ -type transition was observed at 164°C . Stable ZrW_2O_8 phase is depicted in the figure. Heating and cooling rate is $10^\circ\text{C}/\text{min}$.