

Synthesis of Large Amount of Pure Negative-Thermal-Expansion Material, ZrW_2O_8

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Abstract

The preparation method for large amount of negative-thermal-expansion material, ZrW_2O_8 with high purity was developed. It was revealed that the heat-treatment at temperature more than 1200 °C was necessary to prepare ZrW_2O_8 from the mixture of ZrO_2 and WO_3 , resulting in simultaneous evaporation of W during the heat-treatment and residual ZrO_2 in the specimen. Enveloping the pellet composed of mixture of ZrO_2 and WO_3 with Pt foil and/or silica tube to suppress W vaporization was effective to prepare the specimen with high purity. Due to high chemical reactivity between Al and W, alumina was revealed to be unsuitable as a crucible material for preparation of ZrW_2O_8 with solid-state reaction of ZrO_2 and WO_3 . The negative thermal expansion coefficient of prepared ZrW_2O_8 was confirmed with high temperature X-ray diffraction measurement.

Keywords: ZrW_2O_8 , negative thermal expansion, large-scale synthesis, X-ray diffraction, TG-DTA

1. Introduction

Composite materials are widely applied to architecture, energy conversion devices such as solid oxide fuel cells and so on. For a long-term endurance of the composite materials, mismatch of thermal expansion among component materials is regarded to be one of the severe problems. To avoid mechanical destruction due to the mismatch of thermal expansion, method for thermal expansion control is required. Materials with negative thermal expansion coefficient have high potential to solve the problem originated from the mismatch of thermal expansion.

Negative thermal expansion has been reported in several oxides¹⁾. Among them, ZrW_2O_8 has been widely studied because it shows negative thermal expansion for wide temperature range, 0.3 K~900 K²⁻¹⁰⁾. For applica-

tion of ZrW_2O_8 , process in order to prepare specimens with high purity in large scale should be installed. At present, several processes such as solid-state reaction of ZrO_2 and WO_3 ⁶⁻⁹⁾, heat-treatment of co-precipitation powder from aqueous solution of $ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_6H_2W_{12}O_{40}$ ¹⁰⁾ and so on were employed for preparation of ZrW_2O_8 specimens. However, co-precipitation process is not suitable for large-scale synthesis since it takes more than 7 days to prepared ZrW_2O_8 specimens. Solid-state reaction method is suitable for large-scale synthesis; however, several workers reported impurities such as ZrO_2 in the specimens prepared with solid-state reaction of ZrO_2 and WO_3 ^{8,9)}.

In this study, chemical reactivity among ZrO_2 , WO_3 and crucible materials such as Pt, alumina and silica was investigated by X-ray diffraction and TG-DTA measurement in order to develop a process for large-

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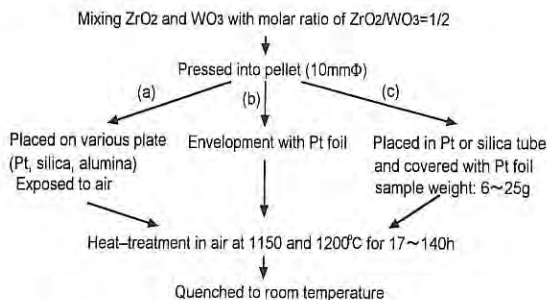


Figure 1 Flow chart of sample preparation

scale synthesis of ZrW_2O_8 with high purity. Method for synthesis of pure ZrW_2O_8 as large as ~ 25 g at one time was developed by improvement of crucible material and preparation conditions.

2. Experimental

2-1. Sample preparation

The sample preparation was carried out by using solid-state reaction of ZrO_2 and WO_3 . Figure 1 depicts three kinds of preparation methods employed in this study. The nominal amount of ZrO_2 and WO_3 powder was mixed in ethanol and pressed into pellet with 10 mm diameter. In the method depicted in Figure 1 (a), the pellets were placed on various plates such as platinum, alumina and silica and heated under open air at the temperatures of 1100°C, 1150°C and 1200°C. The pellets were enveloped with Pt foil prior to the heat-treatment in order to suppress evaporation of component in the process of Figure 1 (b). Large-scale synthesis of ZrW_2O_8 was examined in the process of Figure 1 (c). Several pellets as much as 6~25 g placed in the silica or platinum crucible and covered by platinum foil were heated at 1200°C for 17~140 h. After the heat-treatment, the samples were quenched to room temperature. The phase of the obtained specimens and chemical reactivity of ZrO_2 , WO_3 and crucible materials were analyzed with X-ray diffraction measurements using RINT-2400 (Rigaku Co., Ltd; $CuK\alpha$, 40 kV, 200 mA).

2-2. Evaluation of chemical reactivity with TG-

DTA measurement

In order to evaluate chemical reactivity between ZrO_2 and WO_3 and evaporation of component during the heat-treatment, TG-DTA (thermogravimetry-differential thermal analysis) curves of ZrO_2 , WO_3 and their mixture with ZrO_2/WO_3 molar ratio of 1/2 were measured by using Rigaku TG8120 system. The 50~70 mg of sample powder was set in a Pt pan and subjected to measurement under static air. Some samples were sealed in Pt cell prior to TG-DTA measurement in order to suppress evaporation of the component at high temperature. α -alumina was employed as a reference. TG-DTA curves at temperature range from room temperature to 1200°C were obtained with heating rate of 10°C/min. Successively, the temperature of the TG-DTA apparatus was kept at 1200°C and weight variation by time was recorded.

2-3. Evaluation of thermal expansion coefficient

X-ray diffraction patterns were obtained at various temperatures to determine thermal expansion coefficient of ZrW_2O_8 by using PW3050 system (Philips Japan, Ltd). All the measurements were carried out in air. Temperature range for the measurement was 25~220°C. As the temperature reached the measurement limit, the X-ray diffraction measurement started at intervals of more than 30 min to keep the sample temperature homogeneous.

3. Results and discussion

3-1. Determination of preparation temperature

Figure 2 shows X-ray diffraction patterns of (a) the mixture of ZrO_2 and WO_3 prior to the heat-treatment, the sample which was prepared from the mixture with heat-treatment at (b) 1150°C for 17 h on Pt plate and (c) 1200°C for 17 h on Pt plate. All the X-ray diffraction peaks of Figure 2 (a) could be identified as either ZrO_2 phase or WO_3 one. No difference was observed between X-ray diffraction patterns of Figure 2 (a) and (b), indicating that no chemical reaction occurred between ZrO_2 and WO_3 at 1150°C. Although small amount of ZrO_2 phase was observed, almost all the X-

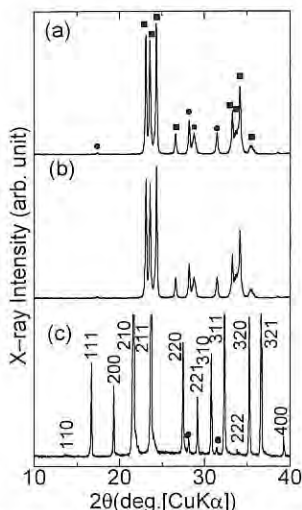


Figure 2 X-ray diffraction patterns of (a) mixture of ZrO_2 and WO_3 , (b) sample prepared with heat-treatment at $1150^\circ C$ for 17h on Pt plate and (c) at $1200^\circ C$ for 17h on Pt plate. ● and ■ indicate peaks of ZrO_2 and WO_3 , respectively. The indexed peaks are identified as ZrW_2O_8 .

ray diffraction peaks depicted in Figure 3 (c) could be indexed assuming cubic symmetry with lattice constant $a=9.155 \text{ \AA}$, indicating that the ZrW_2O_8 phase was prepared with heat-treatment at $1200^\circ C$ ^{3,4}.

Figure 3 shows DTA curve of the mixture of ZrO_2 and WO_3 . Endothermic peak with deviation from base line at $1155^\circ C$ was observed. The peak indicated that the temperature required for the preparation of ZrW_2O_8 from mixture of ZrO_2 and WO_3 was above

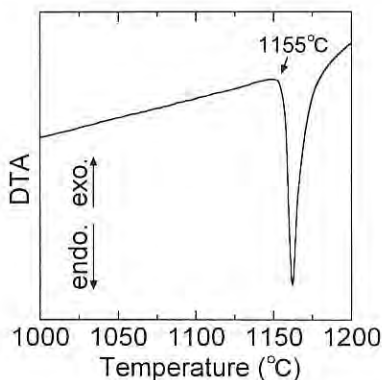


Figure 3 DTA curve of the mixture of ZrO_2 and WO_3 .

$1155^\circ C$, showing correspondence with the results of the X-ray diffraction measurement. Thus, the temperature for preparation of ZrW_2O_8 with solid-state reaction of ZrO_2 and WO_3 was determined to be $1200^\circ C$ in this study.

3 - 2. Optimization of crucible material

Figure 4 shows X-ray diffraction patterns of specimens prepared by heating the mixture of ZrO_2 and WO_3 at $1200^\circ C$ for 17h on (a) Pt plate, (b) silica one and (c) alumina one. Although small peaks originating from ZrO_2 phase was also detected, almost all the X-ray diffraction peaks of the specimen prepared on Pt plate or silica one could be indexed assuming cubic symmetry with lattice constant of $a=9.155 \text{ \AA}$, showing agreement with the crystal structure of ZrW_2O_8 ^{3,4}. This indicated that Pt and silica was suitable for crucible material for preparation of ZrW_2O_8 since they were chemically inert with ZrO_2 , WO_3 and ZrW_2O_8 .

X-ray diffraction pattern of the specimen prepared on alumina plate was different from those prepared on

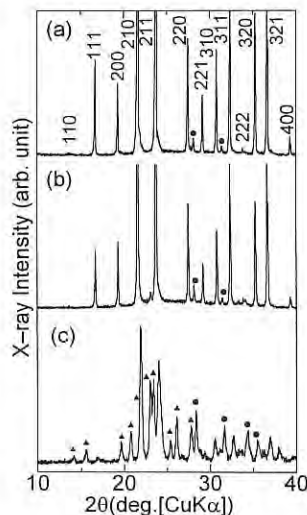


Figure 4 X-ray diffraction patterns of the specimens prepared by heating the mixture of ZrO_2 and WO_3 at $1200^\circ C$ for 17h on (a) Pt plate, (b) silica plate and (c) alumina plate. ● and ▲ represent peaks of ZrO_2 and $Al_2(WO_4)_3$, respectively. Peaks identified as ZrW_2O_8 are indexed in this figure.

Pt plate and silica one. In X-ray diffraction pattern shown in Figure 4 (c), no peak originating from ZrW_2O_8 was observed, instead, peaks identified as $Al_2(WO_4)_3$ and ZrO_2 was observed. It was concluded that the chemical reactivity between Al and W was so high at $1200^\circ C$ that alumina could not be used as crucible material for preparation of ZrW_2O_8 with solid-state reaction of ZrO_2 and WO_3 .

3-3. Preparation of specimen with high purity

As shown in Figure 4 (a) and (b), ZrW_2O_8 single phase was not obtained and small amount of impurity, identified as ZrO_2 , was detected in the specimens prepared with the method depicted in Figure 1 (a). As an origin of residual ZrO_2 , two reasons are probable; (1) Solid-state reaction between ZrO_2 and WO_3 was not completed. (2) Molar ratio of Zr/W increased more than 1/2 during the heat-treatment due to evaporation of WO_3 . According to the phase diagram proposed by Chang and coworkers¹¹, mixture of ZrO_2 and ZrW_2O_8 is stable at $1200^\circ C$ in the region where Zr/W molar ratio is more than 1/2. The latter was more probable than the former because X-ray diffraction peaks originated from WO_3 were not observed as Figure 4 (a) and (b) show.

To verify evaporation of WO_3 , thermogravimetry of ZrO_2 and WO_3 was measured. Figure 5 shows varia-

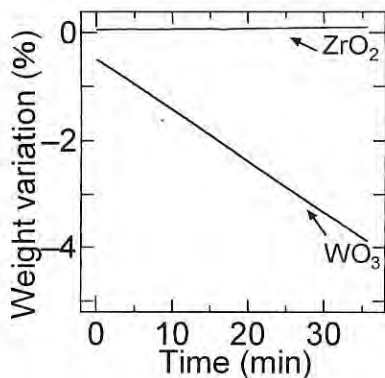


Figure 5 Weight variation of ZrO_2 and WO_3 by time at $1200^\circ C$. The measurements were carried out in air using Pt pan.

tion of weight of ZrO_2 and WO_3 by time at $1200^\circ C$. No weight variation was observed for ZrO_2 , while weight of WO_3 continuously decreased, indicating evaporation of WO_3 .

In order to prepare ZrW_2O_8 specimen with high purity, suppression of WO_3 evaporation is necessary. One of the possible methods is enveloping the pellet prior to heat-treatment. Figure 6 shows weight variation of the mixture of ZrO_2 and WO_3 at $1200^\circ C$ by time with (a) sample exposed to air and (b) sample sealed in Pt cell. Weight decrease could be diminished by enveloping the sample with Pt cell, suggesting that the WO_3 evaporation during the heat-treatment could be suppressed by enveloping the specimen. Weight decrease of the mixture by time at $1200^\circ C$ in sealed Pt cell was supposed to be due to generation of oxygen nonstoichiometry and its verification is now in progress.

Thus, preparation process depicted in Figure 1 (b), in which pellet composed of the mixture of ZrO_2 and WO_3 was enveloped with Pt foil, was examined. Figure 7 shows X-ray diffraction pattern of the obtained specimen heated at $1200^\circ C$ for 17h in air. All the peaks were indexed as cubic symmetry with $a=9.155 \text{ \AA}$, indicating that specimen with ZrW_2O_8 single phase was successfully prepared.

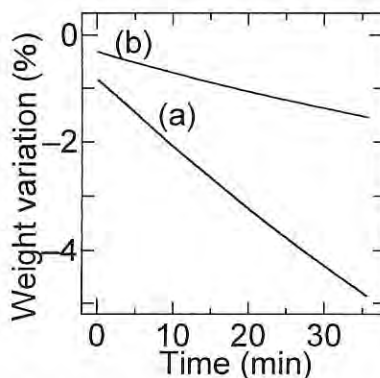


Figure 6 Weight variation of mixture of ZrO_2 and WO_3 by time at $1200^\circ C$. The measurements were carried out with (a) sample exposed to air and (b) sample sealed in Pt cell.

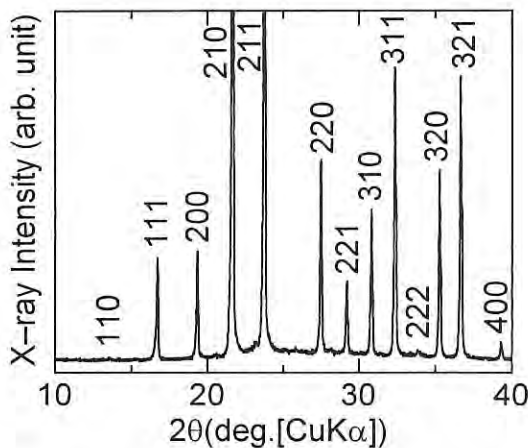


Figure 7 X-ray diffraction pattern of the specimen prepared at 1200°C for 17h in air with sample enveloped by Pt foil. All peaks are indexed as cubic symmetry with $a=9.155 \text{ \AA}$, indicating ZrW_2O_8 single phase.

3 - 4. Large-scale synthesis of ZrW_2O_8 with high purity

As a prototype method for large-scale synthesis, the preparation process depicted in Figure 1 (c) was examined. As a crucible material, Pt or silica was employed for low chemical reactivity with WO_3 at 1200°C. In order to avoid deviation of Zr/W molar ratio during the heat-treatment, the crucible was covered with Pt foil. The heat-treatment was carried out in air at 1200°C, which was determined from the results of DTA measurement. The weight of the specimen obtained at one time was $\sim 25 \text{ g}$. Figure 8 shows X-ray diffraction patterns of the specimens obtained with heat-treatment for (a) 17h and (b) 100h. Although most X-ray diffraction peaks could be indexed as those of ZrW_2O_8 , peaks identified as those of ZrO_2 and WO_3 were also detected in Figure 8 (a), suggesting that chemical reaction between large amount of ZrO_2 and WO_3 was not completed in such a short period. The peaks identified as impurities disappeared with increase of reaction time as shown in Figure 8 (b), indicating that large amount of specimen with ZrW_2O_8 single phase was successfully obtained with the

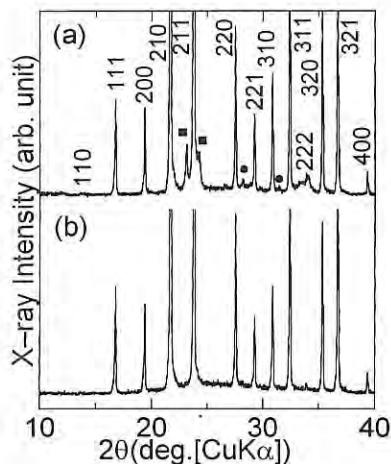


Figure 8 X-ray diffraction patterns of the specimen prepared with the method depicted in Figure 1 (c). The specimens were heat-treated at 1200°C for (a) 17h and (b) 100h. ● and ■ represent peaks of ZrO_2 and WO_3 , respectively. Peaks identified as ZrW_2O_8 are indexed in this figure.

method depicted in Figure 1 (c).

3 - 5. Estimation of thermal expansion coefficient of obtained ZrW_2O_8

The lattice constants of ZrW_2O_8 , prepared with the method shown in Figure 1 (c), at various temperatures were calculated by using 660 diffraction peak. Figure 9 shows temperature dependence of lattice constants. Negative thermal expansion coefficient was observed for temperature range 25~220°C, showing agreement with the results of the preceding studies^{3,4,6}. Discreteness of thermal expansion coefficient was observed at 120~130°C and 160~170°C, which can be attributed to structural phase transition clarified by DSC (differential scanning calorimetry) and high-temperature X-ray diffraction measurement⁶.

4. Conclusion

The process for large-scale synthesis of ZrW_2O_8 with high purity by using solid-state reaction of ZrO_2 and WO_3 was developed. Temperature required for the reaction was determined to be more than 1200°C. Pt and silica were suitable for crucible material, whereas,

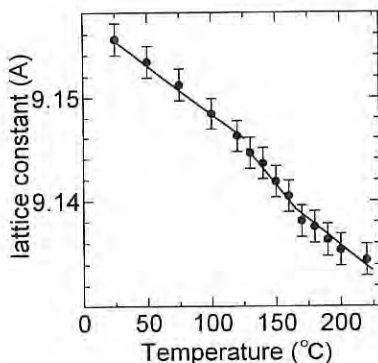


Figure 9 Temperature dependence of lattice constants of ZrW_2O_8 . Negative thermal expansion was confirmed.

alumina was not due to its high chemical reactivity with WO_3 at the temperature. It was clarified that enveloping the specimen in order to suppress WO_3 evaporation was necessary in order to prepare ZrW_2O_8 with high purity.

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