Available online at www.sciencedirect.com
ScienceDirect
Journal of the European Ceramic Society 29 (2009) 3129–3134
www.elsevier.com/locate/jeurceramsoc

Fabrication of zero-thermal-expansion $ZrSiO_4/Y_2W_3O_{12}$ sintered body

I. Yanase *, M. Miyagi, H. Kobayashi

Department of Applied Chemistry, Faculty of Engineering, Saitama University, 255 Shimoohkubo, Saitama 338-8570, Japan

Received 11 February 2009; received in revised form 16 May 2009; accepted 4 June 2009
Available online 1 July 2009

Abstract

We focused on the linear negative thermal expansion of $Y_2W_3O_{12}$ in a wide-temperature range and on the chemical stability of $ZrSiO_4$ in the fabrication of the composite material $ZrSiO_4/Y_2W_3O_{12}$ with a zero-thermal-expansion. The compact composed of $Y_2W_3O_{12}$ and $ZrSiO_4$ had a thermal shrinkage rate smaller than that of $Y_2W_3O_{12}$ and higher than that of $ZrSiO_4$. SEM–EDX observation clarified that the $ZrSiO_4/Y_2W_3O_{12}$ sintered body fabricated at 1400 °C for 10 h had a microstructure composed of $ZrSiO_4$ and $Y_2W_3O_{12}$ grains, and XRD indicated that only $ZrSiO_4$ and $Y_2W_3O_{12}$ phases existed in the sintered body. The relative density of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body reached 92%, which was larger than that of the $ZrSiO_4$ sintered body because $Y_2W_3O_{12}$ grains could be sintered at lower temperatures. The average linear thermal expansion coefficients of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body were -0.4×10^{-6} and -0.08×10^{-6} °C^{-1} in the temperature ranges from 25 to 500 °C and from 25 to 1000 °C, respectively, which showed an almost zero-thermal-expansion.

Keywords: Composites; Thermal expansion; Yttrium tungstate; Zircon; TMA

1. Introduction

Recently, a zero- or near-zero-thermal-expansion property has been required for achieving high precision in modern industries, such as optics, microelectronics and energy transformation, to reduce measurement errors due to thermal deformation in the above fields.[1–3] To meet the above requirements, zero- or near-zero-thermal-expansion materials have been studied. Composite materials have been of interest because they have an advantage in that one can control their thermal expansion coefficients by regulating the chemical compositions of their components.

For instance, ceramic composites fabricated by a reaction sintering process exhibited near-zero-thermal-expansion in the temperature range from RT to 773 K,[4] in which $Fe_{0.2}Sc_{0.8}Mo_3O_{12}$ with a negative thermal expansion coefficient has been dispersed in a MoO_3 matrix with a positive thermal expansion coefficient. However, the composite exhibited positive thermal expansion above 773 K. $BaO–Al_2O_3–B_2O_3$ system glass-ceramics were fabricated[5,6] as materials with a zero or even a negative thermal expansion coefficient, which was smaller than that of glass-ceramics with β-spodumene[7]; however, their near-zero-thermal-expansion temperature region was narrow, that is, from RT to 373 K. $ZrW_2O_8–ZrO_2–Al_2O_3–Al_2(WO_4)_3$ system composites with a near-zero-thermal-expansion coefficient have been reported recently.[8] However, the zero-thermal-expansion behavior changed discontinuously as a function of temperature owing to the structural phase transition of ZrW_2O_8 phase at approximately 430 K. Thus, it has been difficult to develop materials with a zero- or near-zero-thermal-expansion coefficient in a wide-temperature region. Moreover, ceramic materials without glass components are attractive for application at higher temperature.

Yttrium tungstate,[9,10] $Y_2W_3O_{12}$, has a structural type of $A_2M_3O_{12}$[11–14] with orthorhombic symmetry and exhibits an average negative thermal expansion coefficient of -7.0×10^{-6} K^{-1} from 15 to 1373 K. The negative thermal expansion is considered to occur owing to transverse thermal vibrations[12] perpendicular to the Y–O–W linkage of the $Y_2W_3O_{12}$ unit cell. Three lattice parameters, namely, *a*-, *b*-, and *c*-axes of the unit cell, decreased continuously as functions of temperature, which results in a negative thermal expansion of the lattice volume of $Y_2W_3O_{12}$ over the above temperature range.[9] $Y_2W_3O_{12}$ is easily synthesized because it has a more stable phase at RT than ZrW_2O_8, which is necessary for quench

* Corresponding author. Tel.: +81 48 858 3720; fax: +81 48 858 3720.
E-mail address: yanase@apc.saitama-u.ac.jp (I. Yanase).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.06.001

processes in the synthesis of ZrW_2O_8 powders[15,16] and in the fabrication of composites including ZrW_2O_8.[8] Therefore, $Y_2W_3O_{12}$ is attractive as an additive to positive-thermal-expansion materials from the viewpoint of the fabrication of composite materials exhibiting a zero-thermal-expansion.

Zircon, $ZrSiO_4$, is an interesting refractory material for high-temperature applications, having several excellent properties such as chemical stability, low thermal expansion, low thermal conductivity, and high resistance to thermal shock.[17,18] In particular, the chemical stability of zircon is thought to be useful as a matrix phase in the fabrication of composite materials exhibiting zero-thermal-expansion because chemical reactions among components of the composites must be suppressed in the sintering of the composite materials. Therefore, in this study, we focused on the negative thermal expansion of $Y_2W_3O_{12}$ in a wide-temperature range and on the chemical stability of $ZrSiO_4$, and fabricated the composite material $Y_2W_3O_{12}/ZrSiO_4$ with a zero-thermal-expansion.

2. Experimental procedure

2.1. Fabrication

$Y_2W_3O_{12}$ powders were prepared by solid-state reaction. Y_2O_3 (99.9% pure; Wako) and WO_3 (99.9% pure; Wako) powders were mixed in a stoichiometric ratio in ethanol by ball-milling for 24 h. The Y_2O_3 powders were dried in advance at 473 K for 5 h to remove absorbed water molecules. The as-dried mixed powders were shaped into cylindrical pellets of 10 mm diameter and 2 mm thickness by uniaxial pressing at 49 MPa, and then the compacts were heated at 1273 K for 5 h in an aluminum crucible. Here, the compacts were put on pre-prepared $Y_2W_3O_{12}$ powders to prevent the compact from reacting with the alumina crucible. The heated compacts were ground into powders with an agate mortar, and then the resulting $Y_2W_3O_{12}$ powders and commercial $ZrSiO_4$ powders (99% pure; Wako) were mixed with nominal compositions in ethanol by ball-milling for 24 h. The prepared powder mixtures of $Y_2W_3O_{12}$ and $ZrSiO_4$ were shaped into 5 mm × 5 mm × 50 mm compacts by uniaxial pressing at 98 MPa, and the compacts were divided into four equal parts of approximately 5 mm × 5 mm × 12 mm each. The compacts put on pre-prepared $Y_2W_3O_{12}$ powders in an alumina boat were sintered at temperatures of 1473–1673 K for 10 h in air at a heating rate of 5 K/min to fabricate $ZrSiO_4/Y_2W_3O_{12}$ sintered bodies.

2.2. Evaluation

The phases present in the powders and the sintered bodies were investigated by X-ray diffractometry (XRD; Rigaku Rad-C) using Cu Kα radiation within the 2θ range of 15–40°. The bulk densities of $ZrSiO_4$, $Y_2W_3O_{12}$, and $ZrSiO_4/Y_2W_3O_{12}$ sintered bodies were measured by the Archimedes method, with deionized water as the immersion medium. The relative densities of the sintered bodies were calculated using the theoretical densities (4.60 g/cm^3 for $ZrSiO_4$, 4.698 g/cm^3 for $Y_2W_3O_{12}$, and 4.637 g/cm^3 for $ZrSiO_4/Y_2W_3O_{12}$). The relative density of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body with a zero-thermal-expansion was calculated from the mass ratio of $ZrSiO_4/Y_2W_3O_{12} = 1.660$.

The microstructures of the fractured surfaces of the sintered bodies were examined by scanning electron microscopy (SEM; Hitachi S4100) and energy dispersive X-ray analysis (EDX; Quantax400-125S). The thermal shrinkage behaviors of the compacts and the thermal expansion properties of the sintered bodies in the temperature range from 298 to 1273 K were investigated by thermomechanical analysis (TMA; Rigaku, Thermoplus TMA8310) at heating and cooling rates of 5 K/min.

3. Results and discussion

The thermal shrinkage behaviors of the compacts of $Y_2W_3O_{12}$, $ZrSiO_4$, and $ZrSiO_4/Y_2W_3O_{12}$ in the temperature range from RT to 1473 K were investigated by TMA. The results are shown in Fig. 1. The $Y_2W_3O_{12}$ compact began to expand at approximately 323 K and reached around 0.8% in the expansion rate at 473 K, owing to the dehydration of $Y_2W_3O_{12}$.[19,20] The thermal expansion rate of the $Y_2W_3O_{12}$ compact decreased gradually up to 1173 K, and then the compact began to shrink rapidly above 1173 K and reached a 6.0% shrinkage rate at 1473 K. The $ZrSiO_4$ compact showed almost no thermal shrinkage behavior in the temperature range from RT to 1173 K, although it shrank slightly above 1173 K. The $ZrSiO_4/Y_2W_3O_{12}$ compact showed thermal shrinkage with a shrinkage rate lower than that of $Y_2W_3O_{12}$ and higher than that of $ZrSiO_4$. The expansion of the $ZrSiO_4/Y_2W_3O_{12}$ compact in the temperature range from RT to 1173 K was due to the removal of water molecules from $Y_2W_3O_{12}$ in the compact.

The relationships between the sintering temperature and relative density of the sintered bodies of $ZrSiO_4/Y_2W_3O_{12}$, $ZrSiO_4$, and $Y_2W_3O_{12}$ are shown in Fig. 2. The $Y_2W_3O_{12}$ sintered body had a relative density of about 95% at 1473 K, which showed almost no change in the temperature range from 1473 to 1673 K. The high relative density corresponded to the thermal shrinkage

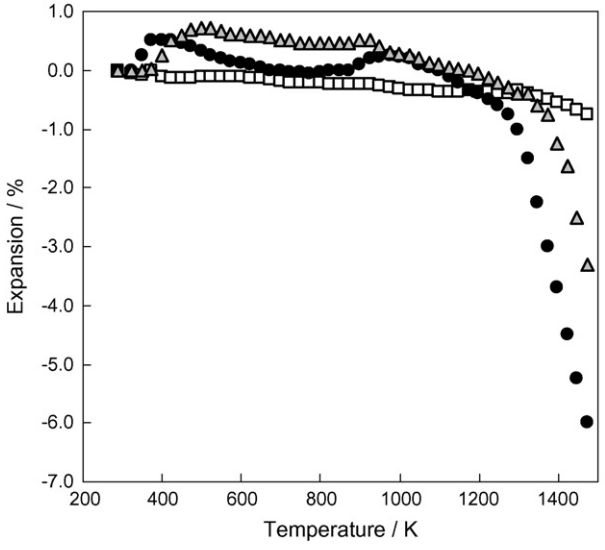

Fig. 1. Thermal shrinkage behaviors in temperature range of 298–1473 K for $Y_2W_3O_{12}$ (●), $ZrSiO_4$ (□), and $Y_2W_3O_{12}/ZrSiO_4$ (△; gray) compacts.

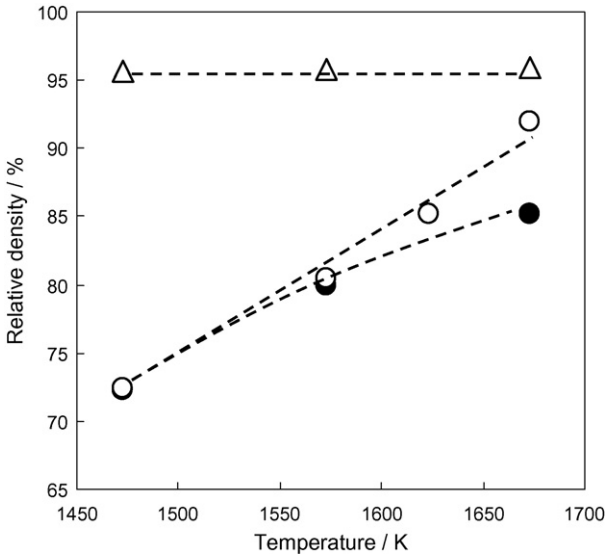

Fig. 2. Relationships between sintering temperature and relative density of $Y_2W_3O_{12}$/$ZrSiO_4$ (◯), $ZrSiO_4$ (●), and $Y_2W_3O_{12}$ (□) sintered bodies fabricated at temperatures of 1473, 1573, and 1673 K for 10 h.

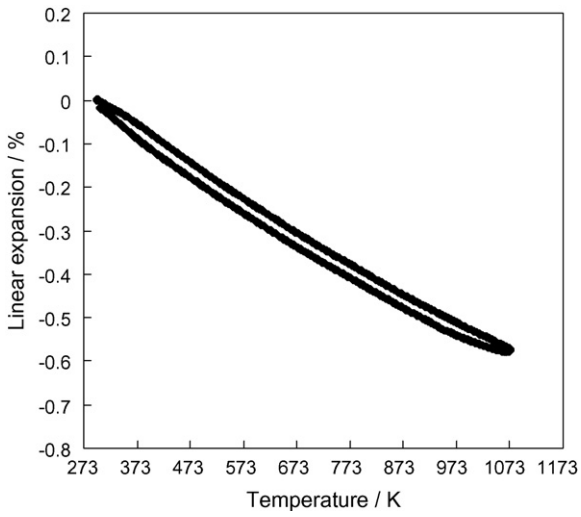

Fig. 4. Thermal expansion property in temperature range from 298 to 1073 K for $Y_2W_3O_{12}$ sintered body fabricated at 1673 K for 10 h.

behavior of $Y_2W_3O_{12}$ shown in Fig. 1, suggesting that $Y_2W_3O_{12}$ could be sintered at low temperatures. The relative density of the $ZrSiO_4$ sintered body increased to about 85% at 1673 K, which was clearly lower than that of $Y_2W_3O_{12}$, and which corresponded to the low shrinkage rate of $ZrSiO_4$, as shown in Fig. 1. The relative density of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body was almost equal to that of the $ZrSiO_4$ sintered body at 1473 and 1573 K, although the shrinkage rate increased gradually, suggesting that the existence of $ZrSiO_4$ grains suppressed the sintering among $Y_2W_3O_{12}$ grains. On the other hand, the relative densities at 1623 and 1673 K of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body were larger than that of the $ZrSiO_4$ sintered body and increased to about 92% at 1673 K, indicating that the sintering among $Y_2W_3O_{12}$ grains proceeded with increasing the sintering temperature.

Fig. 3(a) and (b) shows the fractured surfaces of the $Y_2W_3O_{12}$ sintered body fabricated at 1673 K for 10 h. The densification of the $Y_2W_3O_{12}$ sintered body was recognized from the grains grown in the $Y_2W_3O_{12}$ sintered body. The thermal expansion property of the $Y_2W_3O_{12}$ sintered body was investigated by TMA. The result is shown in Fig. 4. The sintered body showed a negative thermal expansion in the temperature range of RT to 1273 K with a thermal expansion coefficient of $-7.63 \times 10^{-6}\,K^{-1}$, which was almost similar to the report[21] in the temperature range of 473–1073 K.

The fractured surfaces with the porous structure of the $ZrSiO_4$ sintered body, which were fabricated at 1673 K for 10 h, are shown in Fig. 5(a) and (b). The difference between the microstructures of the $Y_2W_3O_{12}$ and $ZrSiO_4$ sintered bodies implies that the $Y_2W_3O_{12}$ compact can be sintered at lower temperatures than the $ZrSiO_4$ compact, corresponding to the thermal shrinkage behaviors of these compacts shown in Fig. 1. The fractured surfaces of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body, which were fabricated at 1673 K for 10 h, are shown in Fig. 6(a) and (b). The microstructure of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body was clearly different from that of the $ZrSiO_4$ sintered body fabricated under the same conditions. From the microstructure of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body, it was considered that the grain growth of $Y_2W_3O_{12}$ occupied space in the porous structure of the $ZrSiO_4$ sintered body, which resulted in the densification of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body.

Fig. 7 shows a SEM image (a) and EDX composition maps (b)–(d) of the microstructure of the $ZrSiO_4$/$Y_2W_3O_{12}$ sintered body fabricated at 1673 K for 10 h. Map (b) is for the

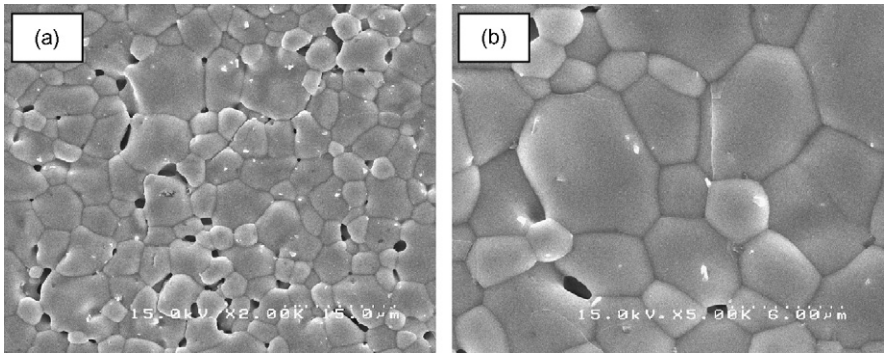

Fig. 3. SEM images of fractured surfaces of $Y_2W_3O_{12}$ sintered body fabricated at 1673 K for 10 h: (a) lower and (b) higher magnifications.

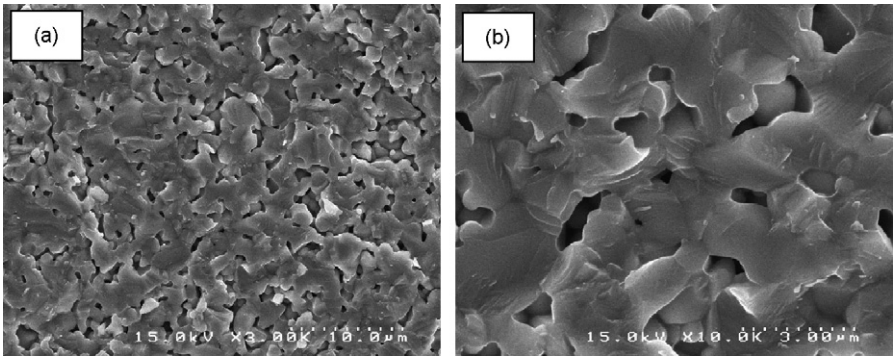

Fig. 5. SEM images of fractured surfaces of $ZrSiO_4$ sintered body fabricated at 1673 K for 10 h: (a) lower and (b) higher magnifications.

distribution of $Y_2W_3O_{12}$ and $ZrSiO_4$ grains, map (c) for that of $ZrSiO_4$ grains, and map (d) for that of $Y_2W_3O_{12\,grains}$. It was observed that the $ZrSiO_4/Y_2W_3O_{12}$ sintered body had the microstructure composed of $ZrSiO_4$ and $Y_2W_3O_{12}$ grains, and that these $ZrSiO_4$ and $Y_2W_3O_{12}$ grains were dispersed. Fig. 8 shows the XRD pattern of the dense $ZrSiO_4/Y_2W_3O_{12}$ sintered body. Only $Y_2W_3O_{12}$ and $ZrSiO_4$ crystalline phases were observed in the sintered body, suggesting that the $Y_2W_3O_{12}$ and $ZrSiO_4$ grains did not react with each other in the sintering process owing to the chemical stability of $ZrSiO_4$.

The thermal expansion property with a slight hysteresis of the dense $ZrSiO_4/Y_2W_3O_{12}$ sintered body is shown in Fig. 9. The thermal expansion rate of the sintered body was almost zero in the temperature range of RT to 1273 K on heating, and the average thermal expansion coefficients were $-0.4 \times 10^{-6}\,K^{-1}$ in the temperature range from 298 to 773 K and $-0.08 \times 10^{-6}\,K^{-1}$ in the temperature range from 298 to 1273 K.

According to Kelly's rule using the volume ratios and thermal expansion coefficients of $ZrSiO_4$ and $Y_2W_3O_{12}$, the mass ratio of $ZrSiO_4/Y_2W_3O_{12} = 1.843$ was considered to be necessary to fabricate a zero-thermal-expansion material, which means that in this study excess $Y_2W_3O_{12}$ was mixed with $ZrSiO_4$ to fabricate the sintered body with a zero-thermal-expansion because a zero-thermal-expansion material could be obtained when the mass ratio was 1.660. Indeed, when the mass ratio of $ZrSiO_4/Y_2W_3O_{12}$ was larger than 1.660, the thermal expansion rate of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body increased, and when it was smaller than 1.660, the thermal expansion rate of the sintered body decreased.

On the other hand, it was noted that the thermal expansion property exhibited a collapsed behavior over the temperature range from RT to 1073 K. This is because the mass ratio of $ZrSiO_4/Y_2W_3O_{12}$ for the fabrication of the compact was calculated using the average linear thermal expansion coefficients in the temperature range from RT to 1273 K although the coefficient of the $Y_2W_3O_{12}$ sintered body increased gradually with increasing temperature, as shown in Fig. 2. Furthermore, the thermal contraction in the temperature range from approximately 1073 to 1173 K and the slight positive thermal expansion above 1173 K were recognized in the thermal expansion property of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body. Sumithra and Umarji reported that the $Y_2W_3O_{12}$ sintered body shows contraction due to creep at high temperatures[19,20] and that creep brings about hysteresis in the thermal expansion of the $Y_2W_3O_{12}$ sintered body. Therefore, the contraction of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body on heating was considered to occur due to the creep of $Y_2W_3O_{12}$ grains in the sintered body in the temperature range from approximately 1073 to 1173 K. The thermal expansion of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body above 1173 K suggests that the positive thermal expansions induced by the $ZrSiO_4$ grains were not successfully suppressed by $Y_2W_3O_{12}$ grains owing to the creep of $Y_2W_3O_{12}$ grains.

Thus, the combination of the creep of $Y_2W_3O_{12}$ and the positive thermal expansion of $ZrSiO_4$ above 1073 K was con-

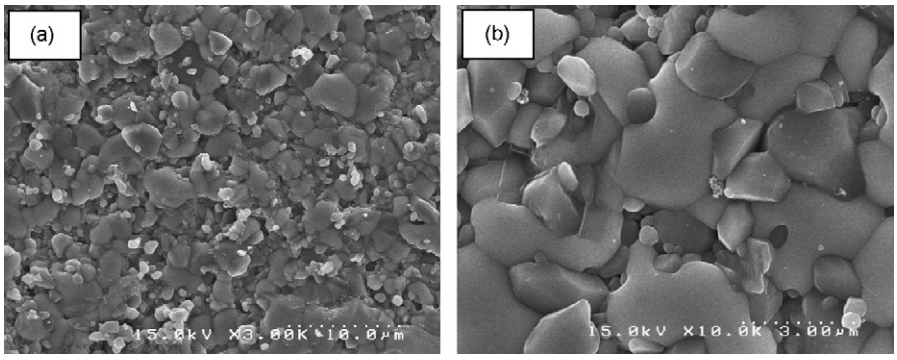

Fig. 6. SEM images of fractured surfaces of $Y_2W_3O_{12}/ZrSiO_4$ sintered body fabricated at 1673 K for 10 h: (a) lower and (b) higher magnifications.

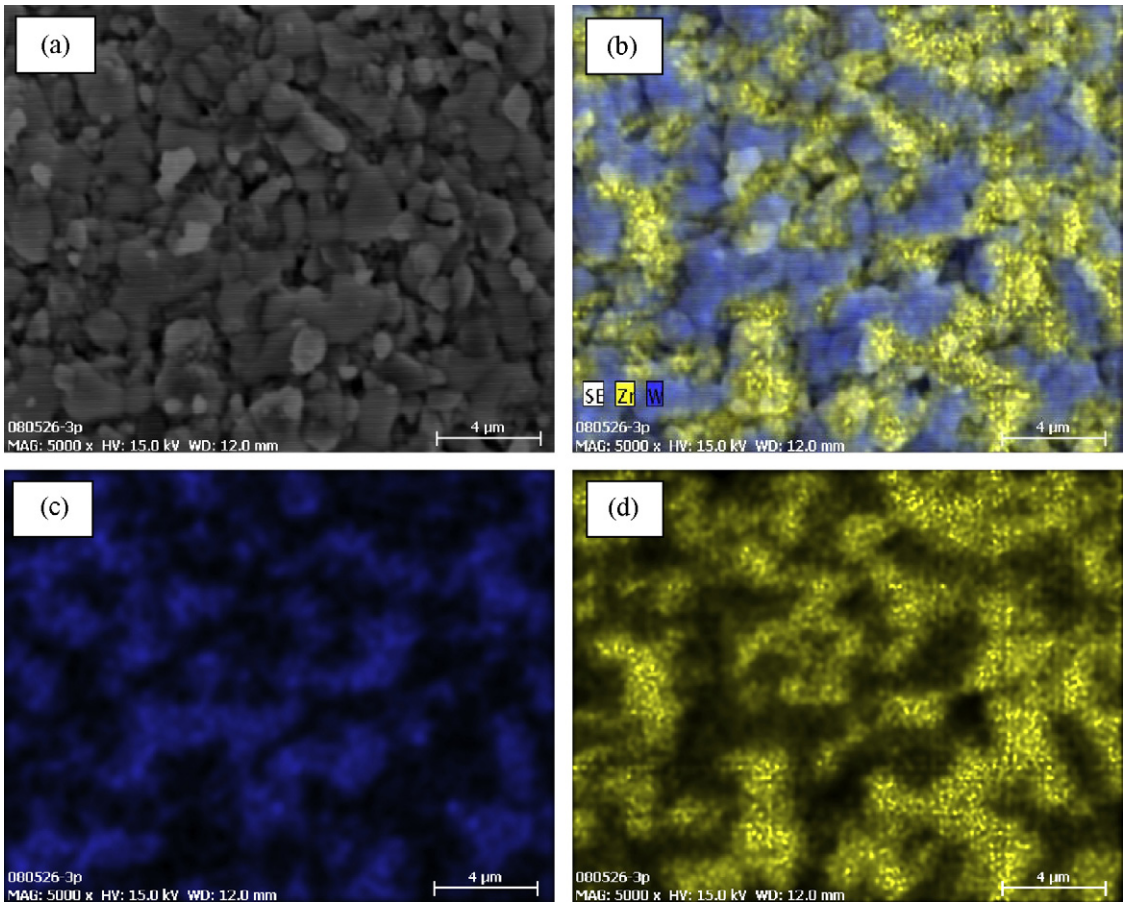

Fig. 7. SEM image (a) of $Y_2W_3O_{12}/ZrSiO_4$ sintered body and EDX composition maps: $Y_2W_3O_{12}$ and $ZrSiO_4$ grains (b), $ZrSiO_4$ grains (c), and $Y_2W_3O_{12}$ grains (d).

sidered to give rise to the slight hysteresis in the thermal expansion curve of the $ZrSiO_4/Y_2W_3O_{12}$ sintered body. However, the dense composite composed of $Y_2W_3O_{12}$ and $ZrSiO_4$ successfully showed an almost zero-thermal-expansion in the temperature range from RT to 1073 K on heating, showing that $ZrSiO_4$ can be an attractive candidate in the fabrication of zero-thermal-expansion materials including negative-thermal-expansion substances.

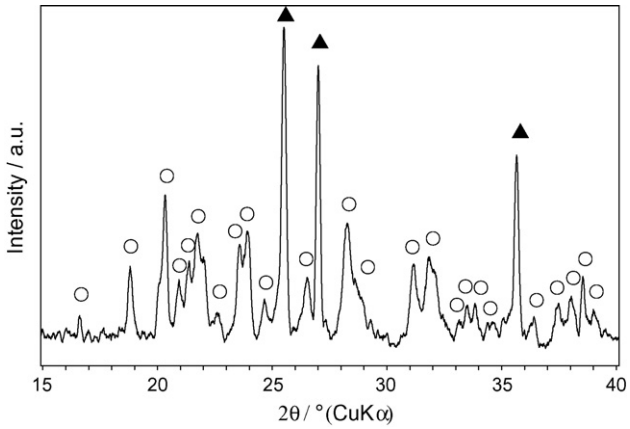

Fig. 8. XRD pattern of $Y_2W_3O_{12}/ZrSiO_4$ sintered body fabricated at 1673 K for 10 h: $Y_2W_3O_{12}$ (◯) and $ZrSiO_4$ (▲).

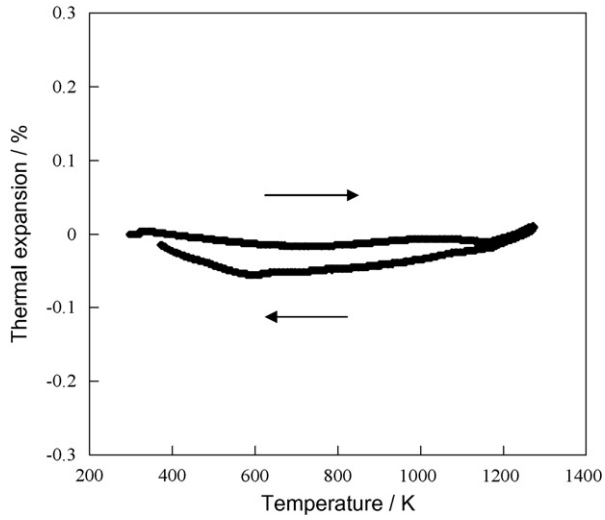

Fig. 9. Thermal expansion property in temperature range of 298–1273 K for $Y_2W_3O_{12}$ sintered body fabricated at 1673 K for 10 h.

4. Conclusions

Composites of $Y_2W_3O_{12}$ and $ZrSiO_4$ were fabricated by sintering at 1673 K for 10 h. The fabricated $Y_2W_3O_{12}/ZrSiO_4$ sintered body had a dense microstructure, and $ZrSiO_4$ and

$Y_2W_3O_{12}$ grains were observed in the microstructure of the dense sintered body. Its XRD pattern indicated that $Y_2W_3O_{12}$ and $ZrSiO_4$ grains did not react with each other in during sintering. The average linear thermal expansion coefficients of the sintered body were $-0.4 \times 10^{-6}\,K^{-1}$ in the temperature range from 298 to 773 K and $-0.08 \times 10^{-6}\,K^{-1}$ in the temperature range from 298 to 1273 K, showing an almost zero-thermal-expansion.

Acknowledgement

This study was supported by Tanigawa Thermal Technology Foundation in Japan.

References

1. Yang, X., Cheng, X., Yan, X., Yang, J., Fu, T. and Qiu, J., Synthesis of ZrO_2/ZrW_2O_8 composites with low thermal expansion. *Compos. Sci. Technol.*, 2007, **67**, 1167–1171.
2. Niwa, E., Wakamoto, S., Ichikawa, T., Wang, S., Hashimoto, T., Takahashi, K. *et al.*, Preparation of dense ZrO_2/ZrW_2O_8 cosintered ceramics with controlled thermal expansion coefficients. *J. Ceram. Soc. Jpn.*, 2004, **112**, 271–275.
3. Namba, Y., Takehara, H. and Nagano, Y., Fracture strength of zero-thermal-expansion glass-ceramics for ultra-precision components. *CIRP Ann. Manuf. Technol.*, 2001, **50**, 239–242.
4. Tran, K. D., Groshens, T. J. and Nelson, J. G., Fabrication of near-zero thermal expansion $(Fe_xSc_{1-x})_2Mo_3O_{12}$–$MoO_3$ ceramic composite using the reaction sintering process. *Mater. Sci. Eng. A*, 2001, **303**, 234–240.
5. Tauch, D. and Russel, C., Glass-ceramics with zero thermal expansion in the system $BaO/Al_2O_3/B_2O_3$. *J. Non-Cryst. Solids*, 2005, **351**, 2294–2298.
6. Tauch, D. and Russel, C., Glass-ceramics in the system $BaO/TiO_2(ZrO_2)/Al_2O_3/B_2O_3$ and their thermal expansion. *J. Non-Cryst. Solids*, 2007, **353**, 2109–2114.
7. Sakamoto, A., Asano, H., Wada, M., Yamamoto, S. and Nishii, J., Mechanical and optical properties of silica glass optical fiber with low-expansion glass-ceramic jacket. *J. Ceram. Soc. Jpn.*, 2003, **111**, 640–644.
8. Sun, L., Sneller, A. and Kwon, P., ZrW_2O_8-containing composites with near-zero coefficient of thermal expansion fabricated by various methods: comparison and optimization. *Compos. Sci. Technol.*, 2008, **68**, 3425–3430.
9. Forster, P. M. and Sleight, A. W., Negative thermal expansion in $Y_2W_3O_{12}$. *Int. J. Inorg. Mater.*, 1999, **1**, 123–127.
10. Koltsova, T. N., X-ray diffraction study of $Y_2W_3O_{12}\cdot 3H_2O$. *Inorg. Mater.*, 2001, **37**, 1175–1177.
11. Wu, M. M., Peng, J., Cheng, Y. Z., Wang, H., Yu, Z. X., Chen, D. F. *et al.*, Structural and thermal expansion properties of solid solution $Nd_{2-x}Eu_xW_3O_{12}$ ($0.0 \leqq \times \leqq 0.6$ and $1.5 \leqq \times \leqq 2.0$). *Solid-State Sci.*, 2006, **8**, 665–670.
12. Evans, J. S. O., Mary, T. A. and Sleight, A. W., Negative thermal expansion in $Sc_2(WO_4)_3$. *J. Solid-State Chem.*, 1998, **137**, 148–160.
13. Forster, P. M., Yokochi, A. and Sleight, A. W., Enhanced negative thermal expansion in $Lu_2W_3O_{12}$. *J. Solid-State Chem.*, 1998, **140**, 157–158.
14. Evans, J. S. O., Mary, T. A. and Sleight, A. W., Negative thermal expansion materials. *Phys. B*, 1998, **241–243**, 311–316.
15. Lommens, P., Meter, C. De., Bruneel, E., Buysser, K. D., Driessche, I. V. and Hoste, S., Synthesis and thermal expansion of ZrO_2/ZrW_2O_8 composites. *J. Eur. Ceram. Soc.*, 2005, **25**, 3605–3610.
16. Morito, Y., Wang, S., Oshima, Y., Uehara, T. and Hashimoto, T., Preparation of dense negative-thermal expansion oxide by rapid quenching of ZrW_2O_8 melt. *J. Ceram. Soc. Jpn.*, 2002, **110**, 544–548.
17. Terki, R., Bertrand, G. and Aourag, H., Full potential investigations of structural and electronic properties of $ZrSiO_4$. *Microelectron. Eng.*, 2005, **81**, 514–523.
18. Veytizou, C., Quinson, J. F. and Jorand, Y., Preparation of zircon bodies from amorphous precursor powder synthesized by sol–gel processing. *J. Eur. Ceram. Soc.*, 2002, **22**, 2901–2909.
19. Sumithra, S. and Umarji, A. M., Hygroscopicity and bulk thermal expansion in $Y_2W_3O_{12}$. *Mater. Res. Bull.*, 2005, **40**, 167–176.
20. Sumithra, S. and Umarji, A. M., Dilatometric studies of $Y_2W_3O_{12}$ with added Al_2O_3. *Proc. Indian Acad. Sci.*, 2003, **115**, 695–701.
21. Sumithra, S., Tyagi, A. K. and Umarji, A. M., Negative thermal expansion in $Eu_2W_3O_{12}$ and $Yb_2W_3O_{12}$ by high temperature X-ray diffraction. *Mater. Sci. Eng. B*, 2005, **116**, 14–18.