

# PREPARATION OF ZrW<sub>2</sub>MoO<sub>8</sub>-CONTAINING COMPOSITES WITH ZERO THERMAL EXPANSION PROPERTY USING Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O AS A SINTERING AID

#QINQIN LIU, CHUNYA FAN, JUNXIONG LIU, HAOHUA LI, XIUJUAN SUN, XIAONONG CHENG

School of Materials Science and Engineering, Jiangsu University,  
Zhenjiang Jiangsu 212013, P. R. China

#E-mail: liu\_qin\_qin@126.com

Submitted June 16, 2015; accepted September 18, 2015

**Keywords:**  $\beta$ -ZrW<sub>2</sub>MoO<sub>8</sub>, Zirconia, Composites, Zero thermal expansion, Sintering aid

*Mixed oxide  $\beta$ -ZrW<sub>2</sub>MoO<sub>8</sub>-containing composites with monoclinic zirconia ( $m$ -ZrO<sub>2</sub>) were prepared in search for zero thermal expansion ceramics over a wide temperature range. Thermomechanical analyzer (TMA) results indicate that the thermal expansion coefficients of the  $\beta$ -ZrW<sub>2</sub>MoO<sub>8</sub>-containing composites decrease with increasing amount of  $\beta$ -ZrW<sub>2</sub>MoO<sub>8</sub> and that the composite with 50 wt. %  $\beta$ -ZrW<sub>2</sub>MoO<sub>8</sub> and 50 wt. %  $m$ -ZrO<sub>2</sub> exhibits near-zero thermal expansion from 30 to about 600°C. However, its relative density is low. The addition of a small amount of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a sintering aid increases the density (possibly because the Al<sup>3+</sup> ion promotes sintering and densification) while affecting the structure and thermal expansion only insignificantly.*

## INTRODUCTION

Generation of stress due to thermal expansion mismatch of component materials should be suppressed in order to increase the mechanical reliability and stability of optical and energy devices. Negative thermal expansion (NTE) materials offer the possibility to solve the problems derived from thermal stress [1].

It has been reported that materials such as cordierite (Mg<sub>2</sub>Al<sub>4</sub>Si<sub>5</sub>O<sub>12</sub>),  $\beta$ -eucryptite (LiAlSi<sub>3</sub>O<sub>8</sub>), ZrV<sub>2-x</sub>P<sub>x</sub>O<sub>7</sub> family and ZrW<sub>2</sub>O<sub>8</sub> family show negative thermal expansion [2]. Among them, ZrW<sub>2</sub>O<sub>8</sub> is regarded as the most promising NTE material for practical application because it shows isotropic NTE from 0.9 to 1050 K [3]. In recent years, ZrW<sub>2</sub>O<sub>8</sub> has been combined with positive thermal expansion materials (Cu [4], Al [5], SnO<sub>2</sub> [6], cement [7] and polyimide [8]) to produce composites with controllable thermal expansion. Unfortunately, the drawback to ZrW<sub>2</sub>O<sub>8</sub> is that its expansion curve shows a discontinuity at around 430 K which is caused by a phase transition from  $\alpha$  to  $\beta$ . This phenomenon changes the coefficient of thermal expansion (CTE) of ZrW<sub>2</sub>O<sub>8</sub> from  $-8.8 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  to  $-4.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [9], which is harmful to the material design as it cause thermal mismatch with matrix whose thermal expansion curve is linear.

ZrW<sub>2</sub>O<sub>8</sub> forms a complete solid solution with ZrMo<sub>2</sub>O<sub>8</sub>, and the  $\alpha$ - $\beta$  phase transition temperature of the ZrW<sub>2-x</sub>Mo<sub>x</sub>O<sub>8</sub> decreases with the substituted content (200K for ZrWMoO<sub>8</sub>) [10]. It is indicated that ZrWMoO<sub>8</sub> may be more suitable to be used as filler to control the composite's CTE since it possesses linear NTE.

ZrO<sub>2</sub> is a very important structural and functional material, but the high CTE ( $10.6 \times 10^{-6} \text{ K}^{-1}$ ) limits its application in precision optical and electronic fields. Some successful attempts to decreasing its CTE have been reported [11-13]. However, a discontinuity caused by  $\alpha$ - $\beta$  phase transition does exist in the thermal expansion curve of ZrO<sub>2</sub>/ZrW<sub>2</sub>O<sub>8</sub> composite, which is undesirable for application [14].

In this study, ZrWMoO<sub>8</sub> is utilized to control the CTE of ZrO<sub>2</sub>. In order to increase the density of the composites, aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) is added as a sintering aid and its effects on the microstructure, phase composition, density and thermal expansion of the fabricated composites are also discussed.

## EXPERIMENTAL

### Preparation of composites

Zr, W, Mo and Al solutions were prepared by dissolving zirconium oxynitrate (ZrO(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O) (analytical reagent) (A.R.), ammonium tungstate (N<sub>5</sub>H<sub>37</sub>W<sub>6</sub>O<sub>24</sub>·H<sub>2</sub>O) (A.R.), ammonium molybdate (N<sub>5</sub>H<sub>37</sub>Mo<sub>6</sub>O<sub>24</sub>·H<sub>2</sub>O) (A.R.) and aluminum nitrate (Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O) (A.R.) in 100, 50, 50 and 5ml distilled water, separately. The raw materials used in ZrO<sub>2</sub>/ZrWMoO<sub>8</sub> composites with different compositions are listed in Table 1. First, W, Mo and Zr solutions were added simultaneously to 25 ml distilled water, and a white precipitate was produced. After that, the procedure can be divided into two cases. For the samples without sintering aid, the

Table 1. Mass fractions and CTEs of the ZrO<sub>2</sub>/β-ZrWMoO<sub>8</sub> composites (XRD intensities are for the -111 and 210 peaks, respectively).

Sample	Mass fraction of ZrWMoO <sub>8</sub> (wt.%) based on the raw materials	I <sub>ZrW<sub>2</sub>O<sub>8</sub></sub>	I <sub>ZrO<sub>2</sub></sub>	Mass fraction w <sub>ZrWMoO<sub>8</sub></sub> (wt. %) determined using quantitative XRD phase analysis	Measured CTE (× 10 <sup>-6</sup> K <sup>-1</sup> )
ZrO <sub>2</sub> -66 % ZrWMoO <sub>8</sub>	66	100	53.1	67.3	-2.811 ± 0.006
ZrO <sub>2</sub> -60 % ZrWMoO <sub>8</sub>	60	100	71.6	60.4	-2.041 ± 0.004
ZrO <sub>2</sub> -50 % ZrWMoO <sub>8</sub>	50	61.8	100	48.3	-0.612 ± 0.003
ZrO <sub>2</sub> -33 % ZrWMoO <sub>8</sub>	33	44.5	100	31.9	1.523 ± 0.005

pH value was set to about 8 during the whole process by adding ammonia or nitric acid. For the samples with sintering aid, Al solution was added to the W, Mo and Zr mixed solution containing white precipitate, and then the pH value was set to 8. The subsequent preparation steps were identical in the two cases. After stirring the mixture solution for another 2 h, aging for 12 h and drying at 80°C, white precursors were obtained. These precursor powders were heat-treated at 600°C for 4 h and then cooled in air. After that, the powders were pressed into cylinders with diameters of 30 mm and height 5 mm and sintered at 1020°C for 1.5 h in air in a closed Pt crucible, and finally quenched in cold water.

#### Characterisation of composites

The samples were characterized by X-ray diffraction (XRD, Rigaku D/max2500). The thermal expansion of the fabricated samples was measured using a thermomechanical analyzer (TMA, NETZSCH DIL 402EP). The microstructure of the samples was observed using a field emission scanning electron microscope (FE-SEM, JSM-7001F), combined with an energy-dispersive spectrometer (EDS). The densities of the sintered samples were determined using the Archimedes principle [15].

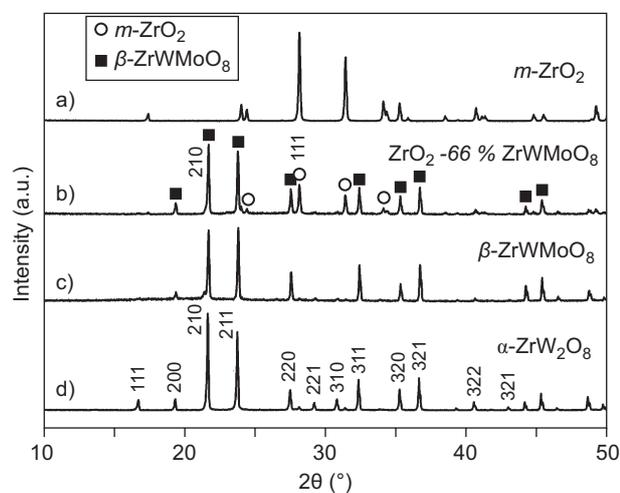


Figure 1. XRD patterns of the fabricated products: a) *m*-ZrO<sub>2</sub>, b) ZrO<sub>2</sub>-66 % ZrWMoO<sub>8</sub>, c) β-ZrWMoO<sub>8</sub> and d) α-ZrW<sub>2</sub>O<sub>8</sub>.

## RESULTS AND DISCUSSION

### Structure characterization and phase composition

Figure 1 shows the XRD pattern of ZrO<sub>2</sub>-66 % ZrWMoO<sub>8</sub> sintered at 1020°C for 1.5 h. The XRD patterns of ZrO<sub>2</sub>, pure β-ZrWMoO<sub>8</sub> and pure α-ZrW<sub>2</sub>O<sub>8</sub> are also shown. It can be seen that there are two phases in the composite; one is ZrO<sub>2</sub> with monoclinic crystal structure (JCPDS 37-1484). The remaining peaks are very similar to those of ZrW<sub>2</sub>O<sub>8</sub> with the cubic structure (JCPDS 50-1865), but the clear absence of the characteristic diffraction peaks (111), (221), (310) and (321) (all systematically absent in *Pa* $\bar{3}$ , but present in *P2*<sub>1</sub><sub>3</sub>) [16] indicates that the other phase adopts the β-ZrW<sub>2</sub>O<sub>8</sub> structure. The results of EDS demonstrate that Mo is part of that phase as well (as expected, since the mole ratio of Mo to W is 1:1), so that it can be indexed as cubic β-ZrWMoO<sub>8</sub> with space group *Pa* $\bar{3}$ . All the results confirm that the composition of the composite is ZrO<sub>2</sub> with monoclinic structure and ZrWMoO<sub>8</sub> with cubic structure.

The XRD patterns of the other samples sintered at 1020°C for 1.5 h are also recorded and are shown in Figure 2, it can be seen that all of the composites' XRD patterns show a two-phase system with a monoclinic ZrO<sub>2</sub> and cubic β-ZrWMoO<sub>8</sub>. The weight ratios of β-ZrWMoO<sub>8</sub> and ZrO<sub>2</sub> are calculated from XRD profiles using a classic quantitative determination of X-ray diffraction method [17]. The value of the constant ( $K_s^{ZrO_2} = 4.89$  and  $K_s^{ZrWMoO_8} = 4.65$ ) is searched from the JCPDS cards, the  $I_{ZrO_2}$  is the intensity of -111 diffraction peaks of ZrO<sub>2</sub> and  $I_{ZrWMoO_8}$  is the intensity of 210 diffraction peaks of ZrWMoO<sub>8</sub>, respectively, see Table 1. The obtained mass fractions

$$w_{ZrWMoO_8} = \frac{1}{1 + K_{ZrO_2}^{ZrWMoO_8} I_{ZrO_2} / I_{ZrWMoO_8}} = 1 \quad (1)$$

$$= \frac{1}{1 + 0.95092 I_{ZrWMoO_8} / I_{ZrO_2}}$$

with  $K_{ZrO_2}^{ZrWMoO_8} = 0.95$  are in very nice agreement with the mass fractions based on the amounts of raw materials used, see Table 1.

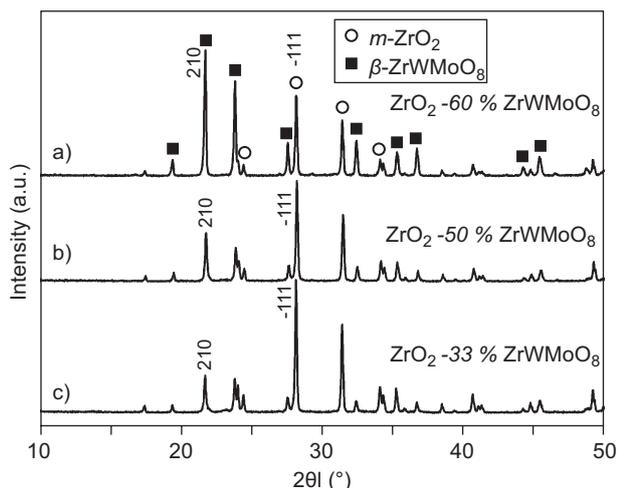


Figure 2. XRD patterns of the fabricated products: a)  $\text{ZrO}_2$ -60 %  $\text{ZrWMoO}_8$ , b)  $\text{ZrO}_2$ -50 %  $\text{ZrWMoO}_8$  and c)  $\text{ZrO}_2$ -33 %  $\text{ZrWMoO}_8$ .

### Thermal expansion

The CTE curves of the fabricated composites are presented in Figure 3. For comparison, the curves of  $m$ - $\text{ZrO}_2$  and  $\beta$ - $\text{ZrWMoO}_8$  are also shown. As can be expected, the CTE of the composites decreases when the  $\beta$ - $\text{ZrWMoO}_8$  to  $\text{ZrO}_2$  ratio increases. By adjusting the mass ratio between  $\beta$ - $\text{ZrWMoO}_8$  and  $\text{ZrO}_2$ , it can be found that the composite with 50 wt. %  $\beta$ - $\text{ZrWMoO}_8$  mass ratio exhibits near zero CTE from 30 to 600°C. The thermal expansion curve of the  $\text{ZrO}_2/\alpha$ - $\text{ZrW}_2\text{O}_8$  composite prepared within our previous research [18] is also shown in Figure 4. It is noteworthy that the shape of the CTE curve of  $\text{ZrO}_2/\beta$ - $\text{ZrWMoO}_8$  composites is different from that of the  $\text{ZrO}_2/\alpha$ - $\text{ZrW}_2\text{O}_8$  composite, the former is linear while the latter varies at about 430 K due to the phase transition of  $\alpha$ - $\text{ZrW}_2\text{O}_8$  [14, 18].

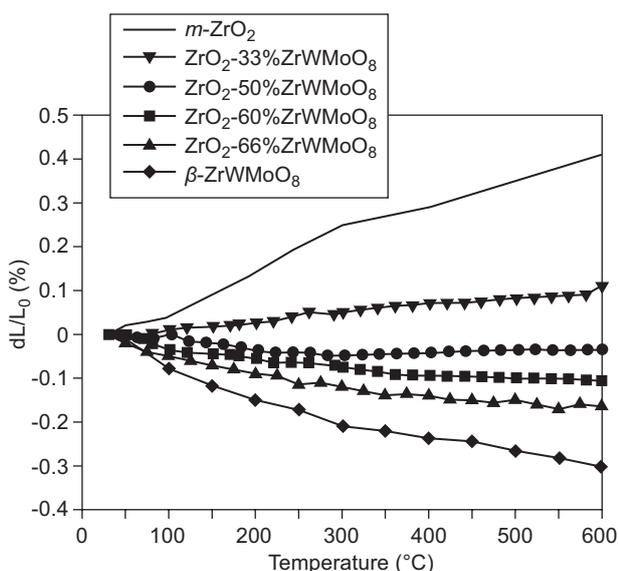


Figure 3. Thermal expansion curves of  $m$ - $\text{ZrO}_2$ , samples listed in Table 1 and  $\beta$ - $\text{ZrWMoO}_8$  from 30 to 600°C.

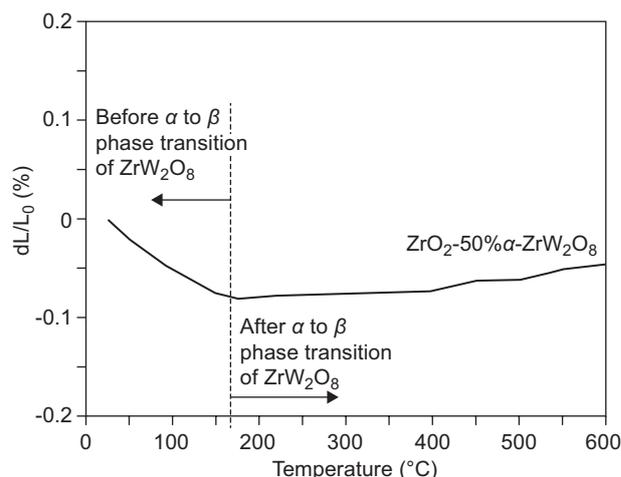


Figure 4. Thermal expansion curve of  $\text{ZrO}_2$ -50 %  $\alpha$ - $\text{ZrW}_2\text{O}_8$  composite prepared within our previous research.

### Influence of sintering aid

The density of  $\text{ZrO}_2$ -50 %  $\text{ZrWMoO}_8$  sample is calculated from the theoretical density values for  $\text{ZrWMoO}_8$  ( $4.97 \text{ g cm}^{-3}$ ) and  $\text{ZrO}_2$  ( $5.83 \text{ g cm}^{-3}$ ). The relative density of  $\text{ZrO}_2$ -50 %  $\text{ZrWMoO}_8$  sample is only 82.3 %, and this low density persists mainly because  $\text{ZrO}_2$  has not been fully sintered. A lot of pores can be seen in the microstructures (Figure 5a). Further observation can find that this composite consists of two different sizes of particles. According to EDS and XRD results, the larger one is  $\text{ZrWMoO}_8$  (marked as A) and the smaller one is  $\text{ZrO}_2$  (marked as B). For  $\text{ZrO}_2$ , a higher sintering temperature (1600°C) is required to obtain dense ceramic [19]. So increasing the sintering temperature may be an efficient ways to increase the density of  $\text{ZrO}_2/\beta$ - $\text{ZrWMoO}_8$  composite ceramics. However, the sintering temperature of  $\text{ZrO}_2/\beta$ - $\text{ZrWMoO}_8$  cannot be increased further due to the fact that pure  $\beta$ - $\text{ZrWMoO}_8$  can only be synthesized in a very narrow temperature range (1173 - 1273K) [20].

It is reported that  $\text{Al}_2\text{O}_3$ , as a sintering aid, can promote the densification of  $\text{ZrO}_2$  ceramics [21]. In the co-precipitation method, aluminum salt can be used as a raw material as it can transform into  $\text{Al}_2\text{O}_3$  in the subsequent reaction process [22]. In order to produce  $\text{ZrO}_2/\beta$ - $\text{ZrWMoO}_8$  composites with high density, different amounts of aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) which is supposed to convert to  $\text{Al}_2\text{O}_3$  in situ is added into the  $\text{ZrO}_2$ -50 %  $\text{ZrWMoO}_8$  composite. The XRD patterns (Figure 6) of specimens with different amount of sintering aid are almost identical, and all the peaks can be indexed as either  $\beta$ - $\text{ZrWMoO}_8$  or  $\text{ZrO}_2$ . There is no indication of an Al-containing compound in the specimens. If present at all, its amount is below the XRD detection limit.

The density of  $\text{ZrO}_2$ -50 %  $\text{ZrWMoO}_8$  composites with different amount sintering aid has been determined

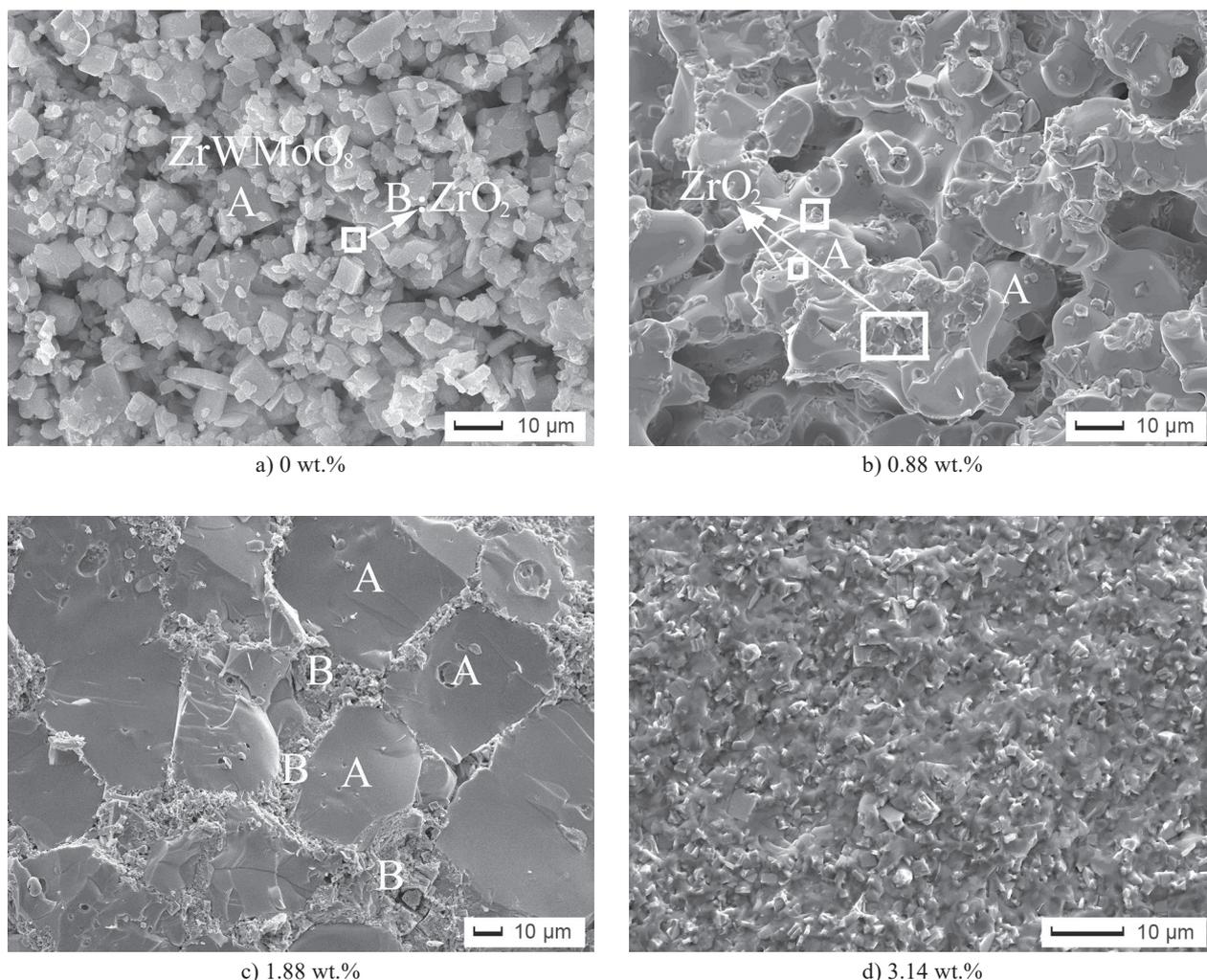


Figure 5. SEM images of  $ZrO_2$ -50 %  $ZrWMoO_8$  composite with different amount of  $Al(NO_3)_3 \cdot 9H_2O$  as sintering aid: a) 0 wt. %, b) 0.88 wt. %, c) 1.88 wt. % and d) 3.14 wt. %.

and the results are shown in Figure 7. It is found that the density increases significantly due to the presence of the sintering aid, but only slightly with the increasing amount of sintering aid. The composite with 3.14 wt. %  $Al(NO_3)_3 \cdot 9H_2O$  possesses the highest density, which higher by 13 % compared to the sample without sintering aid. The increasing compactness is also reflected by their microstructure (Figure 5). Although a few pores still remain in the composite 0.88 wt. %  $Al(NO_3)_3 \cdot 9H_2O$  (Figure 5b), less pores can be seen in the composite with 1.88 wt. %  $Al(NO_3)_3 \cdot 9H_2O$  (Figure 5c). The porosity decreases as the increasing amount of sintering aid. Very few pores can be detected in the composite with 3.14 wt. %  $Al(NO_3)_3 \cdot 9H_2O$  (Figure 5d), so that this composite is almost fully dense. Note that the  $ZrO_2$  particles are not distributed randomly but surround the large  $ZrWMoO_8$  particles.

The CTE-temperature relationship of the composites with  $Al(NO_3)_3 \cdot 9H_2O$  as sintering aid is shown in Figure 8. All specimens show near zero thermal expansion,

implying that the sintering aid  $Al(NO_3)_3 \cdot 9H_2O$  has no significant influence on the near zero thermal expansion.

From these results, it can be concluded that  $Al(NO_3)_3 \cdot 9H_2O$  additive is an very effective sintering aid used in co-precipitation method to improve the density and compactness of  $ZrO_2/\beta$ - $ZrWMoO_8$  composite without influencing near zero thermal expansion. According to our previous research [14], there can be two possible mechanisms. The first is that compounds containing  $Al^{3+}$  and  $Zr^{4+}$  may react and form a solid solution. Thus lattice defects appear which can accelerate the diffusion, promote the sintering process and lead to the increasing density of the composites. The second is that  $Al^{3+}$  reacts with  $WO_3$  and  $MoO_3$  to form  $Al_2(WO_4)_3$  and  $Al_2(MoO_4)_3$ . Of course, the presence of the latter two phases in very small amounts cannot be absolutely excluded, but the amount is definitely too small to be detected by XRD analysis. The existence of the low melting point compounds ( $Al_2(WO_4)_3$  and  $Al_2(MoO_4)_3$ ) could also accelerate the sintering process.

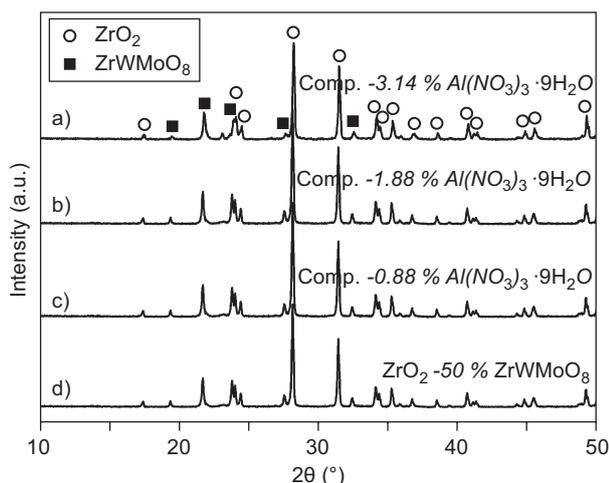


Figure 6. XRD patterns for  $\text{ZrO}_2$ -50%  $\text{ZrWMoO}_8$  composite with different amount of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as a sintering aid (after sintering at  $1020^\circ\text{C}$ ).

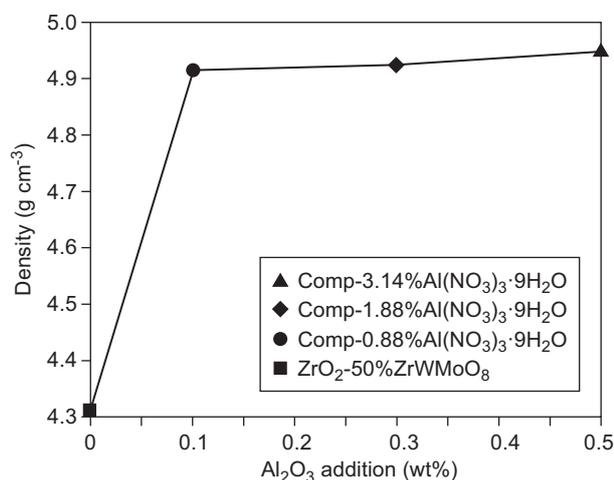


Figure 7. Density for  $\text{ZrO}_2$ -50%  $\text{ZrWMoO}_8$  composite with different amounts of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as a sintering aid.

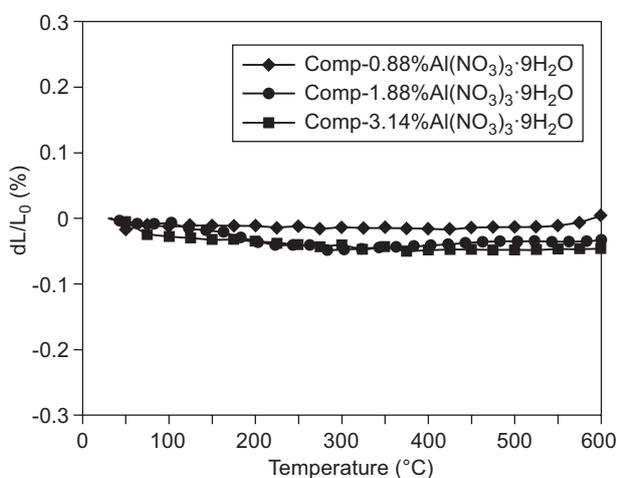


Figure 8. Thermal expansion curves for  $\text{ZrO}_2$ -50%  $\text{ZrWMoO}_8$  composite with different amounts of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  as a sintering aid.

## CONCLUSION

$\text{ZrO}_2/\beta\text{-ZrWMoO}_8$  composites with controllable thermal expansion coefficient were successfully synthesized using a co-precipitation method just by tailoring the mass ratio of raw materials. All composites exhibited an almost linear thermal expansion. The CTE decreases as the mass fraction of the  $\beta\text{-ZrWMoO}_8$  increases. Near-zero thermal expansion was found in the  $\text{ZrO}_2$ -50%  $\text{ZrWMoO}_8$  composite with a mass ratio of 1:1 after sintering. The density can be effectively improved by using aluminum nitrate ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) as a sintering aid which has only a very slight effect on the thermal expansion. It has been suggested that the sintering process is promoted by the lattice defects generated by the extra  $\text{Al}^{3+}$  ions.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 51202093, 51302111 and 51272093), Science Foundation of Jiangsu Province (No. BK20130523).

## REFERENCES

- Pryde A.K.A., Hammonds K.D., Dove M.T., Heine V., Gale J.D., Warren M.W.: *J. Phys. Condens. Matter*. **8**, 10973 (1996).
- Sleight A.W.: *Inorg. Chem.* **37**, 2854 (1998).
- Holzer H., Dunand D.C.: *J. Mater. Res.* **14**, 780 (1999).
- Yilmaz S., Dunand D.C.: *Compos. Sci. Technol.* **64**, 1895 (2004).
- Matsumoto A., Kobayashi K., Nishio T.: *Mater. Sci. Forum* **426**, 2279 (2003).
- Nishiyama S., Yoshida H., Wolfgang T.H.: *Ann. Meet Ceram. Soc. Jap.* **22**, 205 (2002).
- Kofteros M., Rodriguez S., Tandon V., Murr L.E.: *Scripta Mater.* **45**, 369 (2001).
- Lisa M.S., Charles M.L.: *Chem. Mater.* **17**, 2136 (2005).
- Yamamura Y., Nakjima N., Tsuji T.: *Solid State Commun.* **114**, 453 (2000).
- Closmann C., Sleight A.W., Haygarth J.C.: *J. Solid State Chem.* **139**, 424 (1998).
- Eiki N., Shuhji W., Takaaki I., Wang S., Hashimoto T., Takahashi K., Morito Y.: *J. Jpn. Ceram. Soc.* **112**, 271 (2004).
- Lommens P., De Meyer C., Bruneel E., De Buysser K., Van Driessche I., Hoste S.: *J. Eur. Ceram. Soc.* **25**, 3605 (2005).
- Sun L., Sneller A., Kwon P.: *Compos. Sci. Technol.* **68**, 3425 (2008).
- Yang X.B., Cheng X.N.: *Yan X.H.*: *Compos. Sci. Technol.* **67**, 1167 (2007).
- Saddeek Y.B., El Latif L.A.: *Physica B* **348**, 475 (2004).
- Kameswari U., Sleight A.W., Evans J.S.O.: *Inter. J. Inorg. Mater.* **2**, 333 (2000).
- Pawloski G.A.: USA Patent 4592082, 1986.
- Yang X.B., Xu J., Li H.J., Cheng X.N., Yan X.H.: *J. Am. Ceram. Soc.* **90**, 1953 (2007).
- Abden M.J., Afroze J.D., Mamun M.A., Haque M.M.: *Mater. Express* **4**, 317 (2014).
- Zhao R.Q., Yang X.J., Wang H.L.: *J. Solid State Chem.* **180**, 3160 (2007).
- Balmer M.L., Lange F.F., Jayaram V., Carlos G.L.: *J. Am. Ceram. Soc.* **78**, 1489 (1995).
- Han X., Liang Z., Feng L., Wang W., Chen J., Xue C., Zhao H.: *Ceram. Inter.* **41**, 505 (2015).