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Synthesis of $Zr_2WP_2O_{12}/ZrO_2$ Composites with Adjustable Thermal Expansion

Zhiping Zhang[1,2], Weikang Sun[1], Hongfei Liu[1], Guanhua Xie[2], Xiaobing Chen[1,2] and Xianghua Zeng[1]*

[1] Department of Electrical and Mechanical Engineering, Guangling College, Yangzhou University, Yangzhou, China, [2] School of Physiccal Science and Technology, Yangzhou University, Yangzhou, China

$Zr_2WP_2O_{12}/ZrO_2$ composites were fabricated by solid state reaction with the goal of tailoring the thermal expansion coefficient. XRD, SEM and TMA were used to investigate the composition, microstructure, and thermal expansion behavior of $Zr_2WP_2O_{12}/ZrO_2$ composites with different mass ratio. Relative densities of all the resulting $Zr_2WP_2O_{12}/ZrO_2$ samples were also tested by Archimedes' methods. The obtained $Zr_2WP_2O_{12}/ZrO_2$ composites were comprised of orthorhombic $Zr_2WP_2O_{12}$ and monoclinic ZrO_2. As the increase of the $Zr_2WP_2O_{12}$, the relative densities of $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites increased gradually. The coefficient of thermal expansion of the $Zr_2WP_2O_{12}/ZrO_2$ composites can be tailored from 4.1×10^{-6} K^{-1} to -3.3×10^{-6} K^{-1} by changing the content of $Zr_2WP_2O_{12}$. The 2:1 $Zr_2WP_2O_{12}/ZrO_2$ specimen shows close to zero thermal expansion from 25 to 700°C with an average linear thermal expansion coefficient of -0.09×10^{-6} K^{-1}. These adjustable and near zero expansion ceramic composites will have great potential application in many fields.

Keywords: $Zr_2WP_2O_{12}$, ZrO_2, composites, thermal expansion, ceramics

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***Correspondence:**
Hongfei Liu
liuhf@yzu.edu.cn

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INTRODUCTION

Lots of materials known to show positive thermal expansion as temperature increase. In contrast, some materials show completely different thermal expansion properties and contract upon heating. This negative thermal expansion (NTE) phenomena has been found in some $A_2(MO_4)_3$ compounds, where the A cation can be a trivalent main group metal, transition metal, or rare earth element ranging from Lu to Ho, while M corresponds to W or Mo (Sumithra and Umarji, 2004, 2006; Liu H. F. et al., 2012; Liu Q. Q. et al., 2012; Liu et al., 2015). In addition, compounds with aliovalent cations on the A and M site have been reported. For example, $Zr_2WP_2O_{12}$ has been reported to exhibit strong and stable NTE over a wide temperature range. $Zr_2WP_2O_{12}$ adopts the orthorhombic $Sc_2W_3O_{12}$ structure, which consists of ZrO_6 octahedra that share corners with two WO_4 tetrahedra and four PO_4 tetrahedra. Zr-O-W (P) linkages in this structure will lead to the volume contraction due to transverse vibration of bridging oxygen atoms as temperature increase (Isobe et al., 2008, 2009; Cetinkol and Wilkinson, 2009; Tani et al., 2010).

Thermal expansion is an important property of materials, and mismatch in thermal expansion often induces unstable performance or failure of devices in the field of microelectronics, optics and micromachines. To avoid the above problems, control of thermal expansion of materials can be necessary. An easy approach is to mix the NTE material with the positive thermal expansion material in the right proportion.

Most studies describing attempts to synthesize controllable thermal expansion composites mainly focus on ZrW_2O_8 based composites, such as ZrW_2O_8/ZrO_2 (De Buysser et al., 2004; Lommens et al., 2005; Yang et al., 2007; Khazeni et al., 2011; Romao et al., 2015), ZrW_2O_8/Cu and ZrW_2O_8/polyimide (Yilmaz, 2002; Sullivan and Lukehart, 2005; Yang et al., 2010; Hu et al., 2014). The coefficient of thermal expansion (CTE) of the composites drops with the increase of the ZrW_2O_8 filler. However, the cubic NTE phase of ZrW_2O_8 is metastable at room temperature, and has to be prepared by rapid quenching after sintering at 1,200°C. Cubic ZrW_2O_8 show a isotropic NTE over a wide temperature range, but a phase transition from α -ZrW_2O_8 to β -ZrW_2O_8 occurs around 160°C, which leads to the decrease of CTE. This change in thermal expansion may be disadvantageous for composite design. Moreover, when heated to 740°C, ZrW_2O_8 decomposes into ZrO_2 and WO_3 (Mary et al., 1996; Banek et al., 2010; Gao et al., 2016). In addition, cubic ZrW_2O_8 undergoes a pressure induced phase transition to an orthorhombic phase with a positive CTE. This transformation has been observed in composites during thermal cycling, and leads to irreproducible thermal expansion behavior (Perottoni and Jornada, 1998; Miao et al., 2004; Varga et al., 2007; Liu et al., 2014).

$Zr_2WP_2O_{12}$ is a new NTE material for use as a filler to adjust the CTE of ceramics, glasses, metals, and polymers. It exhibits a strong NTE over the broadest temperature range (room temperature to its sublimation point of about 1,600°C). Moreover, it does not suffer from the same limitations as ZrW_2O_8, as it is thermodynamically stable and does not undergo any phase transformations.

The synthesis and NTE behavior of $Zr_2WP_2O_{12}$ ceramics have been reported previously (Isobe et al., 2008, 2009; Cetinkol and Wilkinson, 2009; Tani et al., 2010). $Zr_2WP_2O_{12}$ ceramics show stable NTE with an average linear CET of about -5×10^{-6} K^{-1}. In addition, the $Zr_2WP_2O_{12}$ ceramics display excellent mechanical properties (Isobe et al., 2008, 2009; Cetinkol and Wilkinson, 2009). ZrO_2 ceramics and fibers has been widely used in optics, electronics and high temperature fields (Lommens et al., 2005; Yang et al., 2007). In some special occasions, ZrO_2 need to keep precision dimensional stability with the change in temperature, because a mismatch in size among different precision devices can cause some problems. The average linear CTE of ZrO_2 is about 10×10^{-6} K^{-1} from room temperature to 1,000°C. The absolute values of the CTE of ZrO_2 and $Zr_2WP_2O_{12}$ are thus similar but have opposite signs, suggesting that these materials are good candidates for the preparation of ceramic composites with tunable CTEs. It is beneficial that ZrO_2 does not react with $Zr_2WP_2O_{12}$ at high temperatures, as it is a starting material in the solid state synthesis of $Zr_2WP_2O_{12}$.

A new series of $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites that are expected to show an adjustable CTE were synthesized by a solid state reaction method. This work is devoted to exploring the effects of mass ratio of $Zr_2WP_2O_{12}$ and ZrO_2 on the microstructure, density, and CTE values of the $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites.

TABLE 1 | Synthesis conditions for $ZrO_2/Zr_2WP_2O_{12}$ ceramics.

Mass ratio of $Zr_2WP_2O_{12}$:ZrO_2	m(ZrO_2)/g	m(WO_3)/g	m($NH_4H_2PO_4$)/g
0:1	10	0	0
1:1	6.99	1.87	1.86
2:1	7.18	2.99	2.97
3:1	6.58	3.36	3.34
4:1	5.18	2.99	2.97
1:0	3.97	3.74	3.71

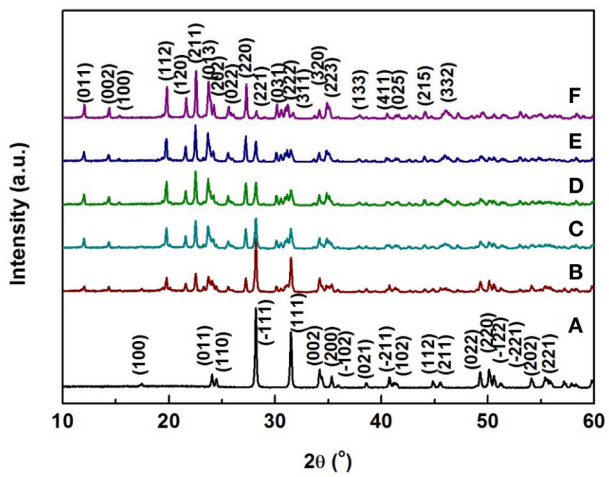

FIGURE 1 | XRD patterns of ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}$-ZrO_2 composites with different mass ratios sintered at 1,200°C for 6 h. **(A)** ZrO_2, **(B)** 1:1 $Zr_2WP_2O_{12}$:ZrO_2, **(C)** 2:1 $Zr_2WP_2O_{12}$:ZrO_2, **(D)** 3:1 $Zr_2WP_2O_{12}$:ZrO_2, **(E)** 4:1 $Zr_2WP_2O_{12}$-ZrO_2, **(F)** $Zr_2WP_2O_{12}$.

EXPERIMENTAL DETAILS

All $Zr_2WP_2O_{12}$, ZrO_2, and $Zr_2WP_2O_{12}/ZrO_2$ ceramics (mass ratios: 1:1, 2:1, 3:1, 4:1) were synthesized through a conventional solid state route. The raw materials were ZrO_2 (Aladdin, purity ≥99.95%), WO_3 (Aladdin, purity ≥99.95%), and $NH_4H_2PO_4$ powders (Aladdin, purity ≥99.5%). A summary of samples prepared can be found in **Table 1**. Reactant mixtures were milled for 6 h to form a homogeneous powder and dried at 80°C, followed by heating at 500°C for 3 h. After this pre-sintering step, the mixtures were uni-axially cold pressed into pellets of 7 mm in diameter and about 2 mm in thickness. Pellets were calcined at 1,200°C in air for 6 h and cooled down in the furnace.

Powder X-ray diffraction experiments were performed on a Shimadzu XRD 7000 using CuKα radiation. Data were collected at 40 kV and 30 mA over the 10° to 60° 2θ range with a scanning speed of 5°/min. The fractured surface morphologies of the samples were observed using a TESCAN VEGA3 scanning electron microscope (SEM). The relative densities of the resulting samples were measured using Archimedes' method. The CTEs of the samples were measured with a Seiko 6300 TMA/SS thermal mechanical analyzer at a heating rate of 5°C/min in air between 25 and 700°C.

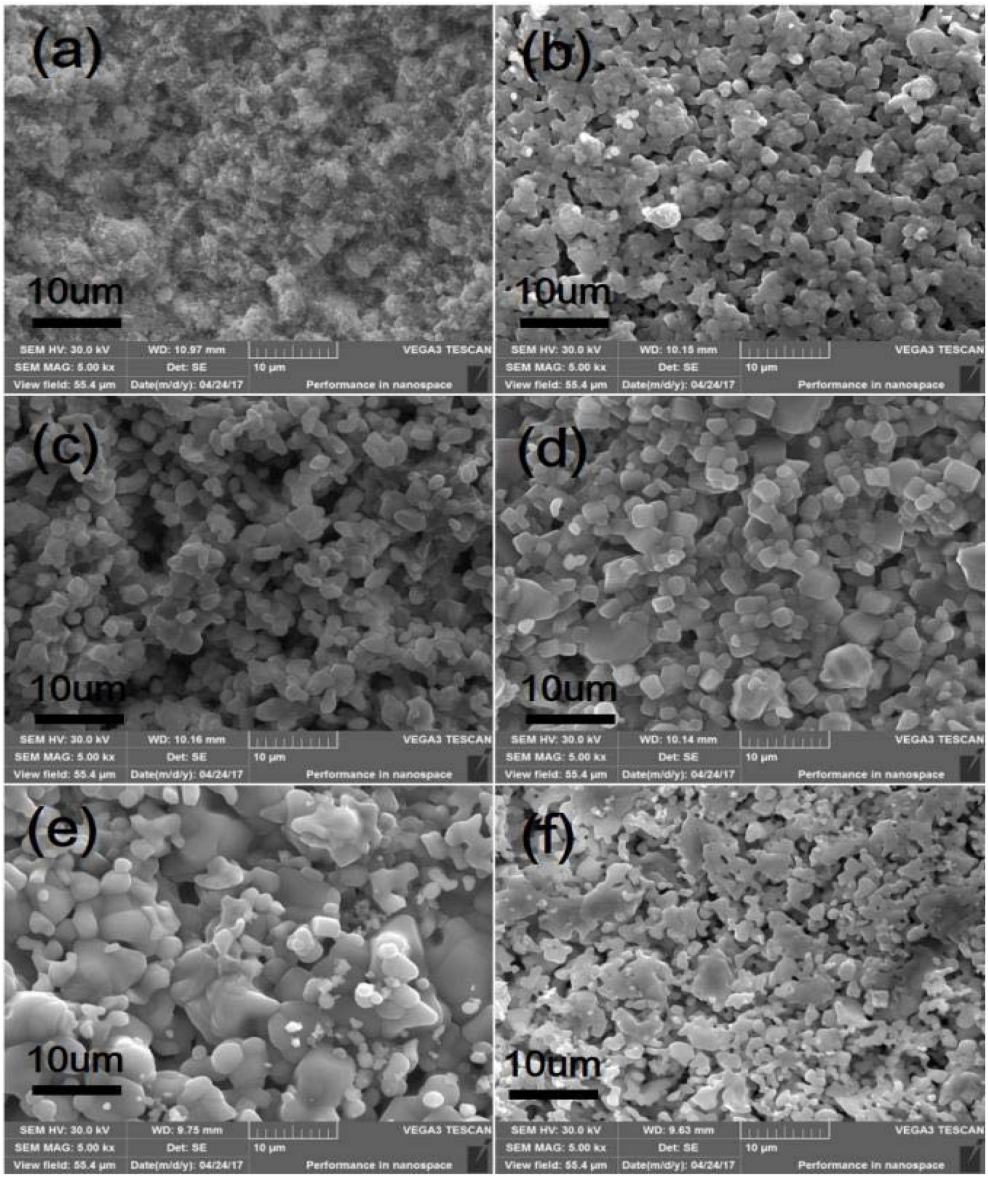

FIGURE 2 | SEM images of ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}$-ZrO_2 composites with different mass ratios sintered at 1,200°C for 6 h, **(a)** ZrO_2, **(b)** 1:1 $Zr_2WP_2O_{12}$:ZrO_2, **(c)** 2:1 $Zr_2WP_2O_{12}$:ZrO_2, **(d)** 3:1 $Zr_2WP_2O_{12}$:ZrO_2, **(e)** 4:1 $Zr_2WP_2O_{12}$-ZrO_2, **(f)** $Zr_2WP_2O_{12}$.

RESULTS AND DISCUSSION

XRD Analysis

Figure 1 shows typical room temperature XRD patterns of $Zr_2WP_2O_{12}/ZrO_2$ composites with different mass ratios synthesized at 1,200°C for 6 h. The XRD patterns of pure ZrO_2 and pure $Zr_2WP_2O_{12}$ ceramics are also displayed for reference. For pure ZrO_2 ceramics (**Figure 1A**), all observed reflections could be well indexed and attributed to monoclinic ZrO_2 in agreement with JCPDS card number 65–1,023. For pure $Zr_2WP_2O_{12}$ ceramics (**Figure 1F**), all diffraction peaks matched those expected for orthorhombic $Zr_2WP_2O_{12}$ (JCPDS 43-0258). No impurity phases were detected. XRD patterns of $Zr_2WP_2O_{12}/ZrO_2$ composites with mass ratios of 1:1, 2:1, 3:1, and 4:1 (**Figures 1B–E**) displayed diffraction peaks belonging to both monoclinic ZrO_2 and orthorhombic $Zr_2WP_2O_{12}$. As no intermediate phase exists between ZrO_2 and $Zr_2WP_2O_{12}$, no reaction can occur between excess ZrO_2 and $Zr_2WP_2O_{12}$. As expected, the diffraction peaks of $Zr_2WP_2O_{12}$ became more intense with increasing mass ratio of $Zr_2WP_2O_{12}$.

SEM and Density Analysis

SEM micrographs of different weight ratio $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites, ZrO_2 and $Zr_2WP_2O_{12}$ ceramics after sintering at 1,200°C for 6 h are shown in **Figure 2**. The SEM

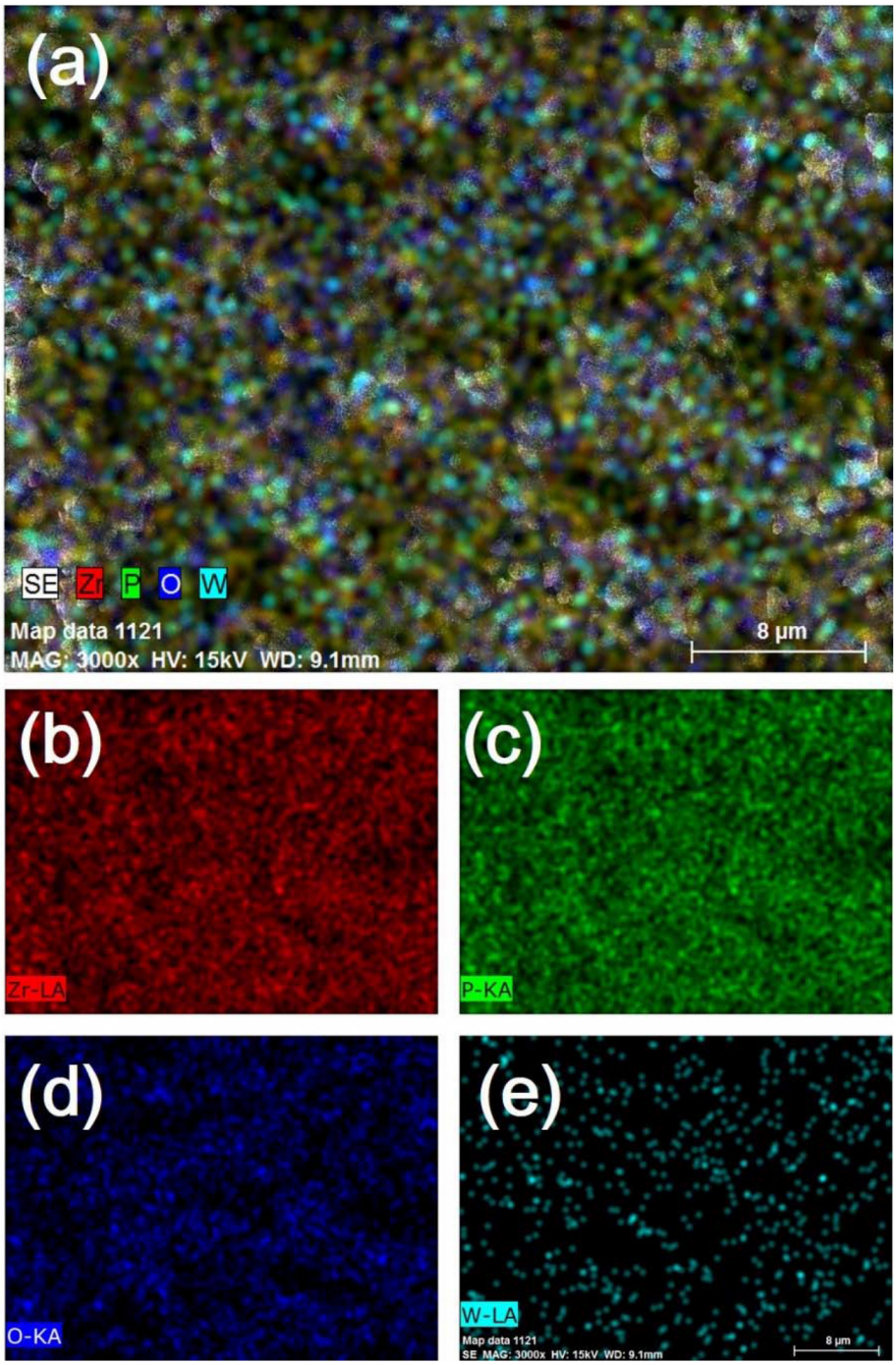

FIGURE 3 | EDX composition maps **(a)** Zr, P, W and O, **(b)** Zr, **(c)** P, **(d)** O, and **(e)** W analysis for 2:1 $Zr_2WP_2O_{12}$:ZrO_2 composite.

image of the ZrO_2 ceramics (**Figure 2a** revealed significant porosity, which is likely due to insufficient sintering. It is known that the sintering temperature required to fabricate dense and tough ZrO_2 ceramics is higher than 1,400°C (Varga et al., 2007). **Figures 2b–e** show SEM images of sintered $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites as a function of different mass ratios. With increasing amount of $Zr_2WP_2O_{12}$, $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites sintered for the same time at the same temperature became denser and displayed larger grain sizes and less porosity. The average grain size of 1:1 $Zr_2WP_2O_{12}/ZrO_2$ composites was about 2–3 µm, but increased to about 6–8 µm when the mass ratio of $Zr_2WP_2O_{12}/ZrO_2$ was increased to 4:1. Pure $Zr_2WP_2O_{12}$

TABLE 2 | Relative densities of ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}$-ZrO_2 composites with different mass ratios.

Sample	Relative density (%)
ZrO_2	74.5
1:1 $Zr_2WP_2O_{12}$-ZrO_2	84.1
2:1 $Zr_2WP_2O_{12}$-ZrO_2	85.5
3:1 $Zr_2WP_2O_{12}$-ZrO_2	89.8
4:1 $Zr_2WP_2O_{12}$-ZrO_2	91.5
$Zr_2WP_2O_{12}$	79.7

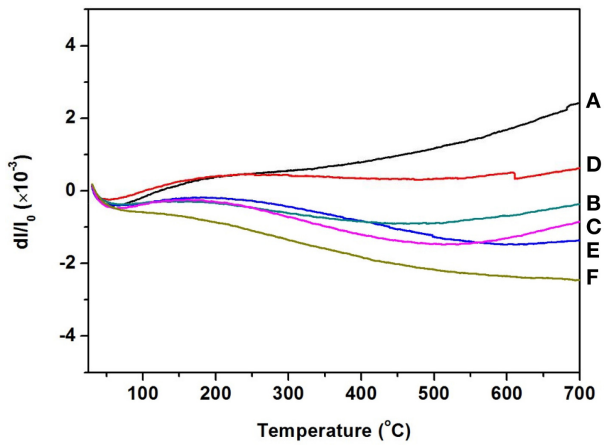

FIGURE 4 | Thermal expansion curves of ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}$-ZrO_2 composites. **(A)** ZrO_2, **(B)** 1:1 $Zr_2WP_2O_{12}$:ZrO_2, **(C)** 2:1 $Zr_2WP_2O_{12}$:ZrO_2, **(D)** 3:1 $Zr_2WP_2O_{12}$:ZrO_2, **(E)** 4:1 $Zr_2WP_2O_{12}$-ZrO_2, **(F)** $Zr_2WP_2O_{12}$.

TABLE 3 | Average linear thermal expansion coefficients of ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}$-ZrO_2 composites in corresponding testing temperature range from 25 to 700°C.

Samples	Coefficient of thermal expansion
ZrO_2	4.10×10^{-6} K^{-1}
1:1 $Zr_2WP_2O_{12}$-ZrO_2	1.32×10^{-6} K^{-1}
2:1 $Zr_2WP_2O_{12}$-ZrO_2	-0.09×10^{-6} K^{-1}
3:1 $Zr_2WP_2O_{12}$-ZrO_2	-0.88×10^{-6} K^{-1}
4:1 $Zr_2WP_2O_{12}$-ZrO_2	-1.50×10^{-6} K^{-1}
$Zr_2WP_2O_{12}$	-3.30×10^{-6} K^{-1}

(**Figure 2f**) showed a wide size distribution of spherical grains with some residual porosity, which is in agreement with results reported earlier (Isobe et al., 2008, 2009; Cetinkol and Wilkinson, 2009). **Figure 3** shows the composition maps analysis of the 2:1 $Zr_2WP_2O_{12}$:ZrO_2 composite. Homogeneous spatial distributions of Zr, P, W, and O elements were observed. These results indicates that $Zr_2WP_2O_{12}$ and ZrO_2 phase uniformly distributed as expected.

In this work, the densities of the resulting $Zr_2WP_2O_{12}$, ZrO_2, and $Zr_2WP_2O_{12}/ZrO_2$ (mass ratio: 1:1, 2:1, 3:1, 4:1) ceramics were also measured using Archimedes' technique. The relative densities were calculated from theoretical values for $Zr_2WP_2O_{12}$ (3.63 g/cm^3) and ZrO_2 (5.817 g/cm^3). As shown in **Table 2**, the results are consistent with the SEM analysis above. The relative densities of pure $Zr_2WP_2O_{12}$ and ZrO_2 were low, however, the densities of $Zr_2WP_2O_{12}/ZrO_2$ (mass ratio: 1:1, 2:1, 3:1, 4:1) ceramics increased with increasing content of $Zr_2WP_2O_{12}$. For a 4:1 mass ratio $Zr_2WP_2O_{12}/ZrO_2$ composite, the relative density of the sample reached 91.5% of the theoretical density values. The sintering temperature of $Zr_2WP_2O_{12}$ is lower than that of ZrO_2, which results in a decreased sintering temperature and better densification of $Zr_2WP_2O_{12}/ZrO_2$ ceramics with increasing content of $Zr_2WP_2O_{12}$.

Thermal Expansion Analysis

Figure 4 gives the information about the thermal expansion of all the $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites synthesized at 1,200°C for 6 h. For purposes of comparison, the thermal expansion curves of pure ZrO_2 and pure $Zr_2WP_2O_{12}$ ceramics are also given in **Figure 4**. Average linear CTEs of the obtained ZrO_2, $Zr_2WP_2O_{12}$, and $Zr_2WP_2O_{12}/ZrO_2$ ceramics with different mass ratios are summarized in **Table 3**. Pure ZrO_2 ceramics (**Figure 4A**) showed positive thermal expansion between 25 and 700°C, and the average linear CTE was measured to be 4.1×10^{-6} K^{-1}, which is lower than the value reported in the literature (Lommens et al., 2005; Yang et al., 2007). This is likely due to insufficient sintering of the ZrO_2 ceramics, as some of the expansion can be absorbed by the empty pore space. Pure $Zr_2WP_2O_{12}$ ceramics (**Figure 4F**) showed NTE in the testing temperature range. The average linear CTE of the $Zr_2WP_2O_{12}$ ceramics was measured to be -3.3×10^{-6} K^{-1} in the temperature range of 25–700°C, which is consistent with literature reports (Cetinkol and Wilkinson, 2009; Isobe et al., 2009). As can be expected, the CTEs of the $Zr_2WP_2O_{12}/ZrO_2$ composites decreased from 4.1×10^{-6} K^{-1} to -3.3×10^{-6} K^{-1} as the weight fraction of $Zr_2WP_2O_{12}$ was increased. As shown in **Figure 4C**, the 2:1 $Zr_2WP_2O_{12}/ZrO_2$ specimen showed close to zero thermal expansion with an average linear CTE of -0.09×10^{-6} K^{-1} in the temperature range of 25–700°C. This near zero expansion ceramic composite will have a number of potential applications in many fields. These results suggest that the CTE of the $Zr_2WP_2O_{12}$-ZrO_2 composites can be modified in the range from 4.1×10^{-6} K^{-1} to -3.3×10^{-6} K^{-1}, and that it is even possible to achieve zero thermal expansion by adjusting the mass ratios of $Zr_2WP_2O_{12}$ and ZrO_2.

CONCLUSIONS

$Zr_2WP_2O_{12}/ZrO_2$ ceramic composites with adjustable thermal expansion coefficients were successfully fabricated by a solid state reaction method. The composites consisted of orthorhombic $Zr_2WP_2O_{12}$ and monoclinic ZrO_2 with no intermediate phases observed. With increasing amount of $Zr_2WP_2O_{12}$, the relative densities of the $Zr_2WP_2O_{12}/ZrO_2$ ceramic composites increased gradually. The CTE of the $Zr_2WP_2O_{12}/ZrO_2$ composites can be tailored from 4.1×10^{-6} K^{-1} to -3.3×10^{-6} K^{-1} by changing the weight fraction of $Zr_2WP_2O_{12}$. For a mass ratio of $Zr_2WP_2O_{12}/ZrO_2$ of 2:1, the $Zr_2WP_2O_{12}/ZrO_2$ ceramic

composite showed close to zero thermal expansion with an average linear CTE of -0.09×10^{-6} K^{-1} between 25 and 700°C.

AUTHOR CONTRIBUTIONS

HL, XC, and ZZ designed experiments; WS and GX carried out experiments; HL, ZZ, and XZ analyzed experimental results and wrote the manuscript.

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REFERENCES

Banek, N. A., Baiz, H. I., Latigo, A., and Lind, C. (2010). Autohydration of nanosized cubic zirconium tungstate. *J. Am. Chem. Soc.* 132, 8278–8279. doi: 10.1021/ja101475f

Cetinkol, M., and Wilkinson, A. P. (2009). Pressure dependence of negative thermal expansion in $Zr_2(WO_4)(PO_4)_2$. *Solid State Commun.* 149, 421–424. doi: 10.1016/j.ssc.2009.01.002

De Buysser, K., Lommens, P., De Meyer, C., Bruneel, E., Hoste, S., and Driessche, I. V. (2004). ZrO_2-ZrW_2O_8 composites with tailor-made thermal expansion. *Ceram. Silikaty* 48, 139–144.

Gao, X., Coleman, M. R., and Lind, C. (2016). Surface modification of ZrW_2O_8 and $ZrW_2O_7(OH)_2{\cdot}2H_2O$ filler particles for controlled thermal expansion polycarbonate composites. *Pol. Comp.* 37, 1359–1368. doi: 10.1002/pc.23304

Hu, L., Chen, J., Fan, L. L., Ren, Y., Rong, Y. C., Pan, Z., et al. (2014). Zero thermal expansion and ferromagnetism in cubic $Sc_{1-x}M_xF_3$ (M= Ga, Fe) over a wide temperature range. *J. Am. Chem. Soc.* 136, 13566–13569. doi: 10.1021/ja5077487

Isobe, T., Kato, Y., Mizutani, M., Ota, T., and Daimon, K. (2008). Pressureless sintering of negative thermal expansion $ZrW_2O_8/Zr_2WP_2O_{12}$ composites. *Mater. Lett.* 62, 3913–3915. doi: 10.1016/j.matlet.2008.05.046

Isobe, T., Umezome, T., Kameshima, Y., Nakajima, A., and Okada, K. (2009). Preparation and properties of negative thermal expansion $Zr_2WP_2O_{12}$ ceramics. *Mater. Res. Bull.* 44, 2045–2049. doi: 10.1016/j.materresbull.2009.07.020

Khazeni, N., Mavis, B., Gunduz, G., and Colak, U. (2011). Synthesis of zirconium tungstate-zirconia core-shell composite particles. *Mater. Res. Bull.* 46, 2025–2031. doi: 10.1016/j.materresbull.2011.07.006

Liu, H. F., Pan, K. M., Jin, Q., Zhang, Z. P., Wang, G., and Zeng, X. H. (2014). Negative thermal expansion and shift in phase transition temperature in Mo-substituted ZrW_2O_8 thin films prepared by pulsed laser deposition. *Ceram. Int.* 40, 3873–3878. doi: 10.1016/j.ceramint.2013.08.028

Liu, H. F., Zhang, W., Zhang, Z. P., and Chen, X. B. (2012). Synthesis and negative thermal expansion properties of solid solutions $Yb_{2-x}La_xW_3O_{12}$ ($0 \leq x \leq 2$). *Ceram. Int.* 38, 2951–2956. doi: 10.1016/j.ceramint.2011.11.072

Liu, H. F., Zhang, Z. P., Ma, J., Zhu, J., and Zeng, X. H. (2015). Effect of isovalent substitution on phase transition and negative thermal expansion of $In_{2-x}Sc_xW_3O_{12}$ ceramics. *Ceram. Int.* 41, 9873–9877. doi: 10.1016/j.ceramint.2015.04.062

Liu, Q. Q., Yang, J., Cheng, X. N., Liang, G. S., and Sun, X. J. (2012). Preparation and characterization of negative thermal expansion $Sc_2W_3O_{12}$/Cu core–shell composite. *Ceram. Int.* 38, 541–545. doi: 10.1016/j.ceramint.2011.07.041

Lommens, P., Meyer, C. D., Bruneel, E., Buysser, K. D., Driessche, I. V., and Hoste, S. (2005). Synthesis and thermal expansion of ZrO_2/ZrW_2O_8 composites. *J. Eur. Ceram. Soc.* 25, 3605–3610. doi: 10.1016/j.jeurceramsoc.2004.09.015

Mary, T. A., Evans, J. S. O., Vogt, T., and Sleight, A. W. (1996). Negative thermal expansion from 0.3 K to 1050 K in ZrW_2O_8. *Science* 272, 90–92. doi: 10.1126/science.272.5258.90

Miao, X. G., Sun, D., Hoo, P. W., Liu, J. L., Hu, Y. F., and Chen, Y. M. (2004). Effect of titania addition on yttria-stabilised tetragonal zirconia ceramics sintered at high temperatures. *Ceram. Int.* 30, 1041–1047. doi: 10.1016/j.ceramint.2003.10.025

Perottoni, C. A., and Jornada, J. A. H. (1998). Pressure-induced amorphization and negative thermal expansion in ZrW_2O_8. *Science* 280, 886–888. doi: 10.1126/science.280.5365.886

Romao, C. P., Marinkovic, B. A., Werner-Zwanzige, U., and White, M. A. (2015). Thermal expansion reduction in alumina-toughened zirconia by incorporation of zirconium tungstate and aluminum tungstate. *J. Am. Chem. Soc.* 98, 2858–2865. doi: 10.1111/jace.13675

Sullivan, L. M., and Lukehart, C. M. (2005). Zirconium tungstate (ZrW_2O_8)/polyimide nanocomposites exhibiting reduced coefficient of thermal expansion. *Chem. Mater.* 17, 2136–2141. doi: 10.1021/cm0482737

Sumithra, S., and Umarji, A. M. (2004). Role of crystal structure on the thermal expansion of $Ln_2W_3O_{12}$ (Ln =La, Nd, Dy, Y., Er and Yb). *Solid State Sci.* 6, 1313–1319. doi: 10.1016/j.solidstatesciences.2004.07.023

Sumithra, S., and Umarji, A. M. (2006). Negative thermal expansion in rare earth molybdates. *Solid State Sci.* 8, 1453–1458. doi: 10.1016/j.solidstatesciences.2006.03.010

Tani, J., Takahashi, M., and Kido, H. (2010). Fabrication and thermal expansion properties of $ZrW_2O_8/Zr_2WP_2O_{12}$ composites. *J. Eur. Ceram. Soc.* 30, 1483–1488. doi: 10.1016/j.jeurceramsoc.2009.11.010

Varga, T., Lind, C., Wilkinson, A. P., Xu, H., Lesher, C. E., and Navrotsky, A. (2007). Heats of formation for several crystalline polymorphs and pressure-induced amorphous forms of AMo_2O_8 (A=Zr, Hf) and ZrW_2O_8. *Chem. Mater.* 19, 468–476. doi: 10.1021/cm0617743

Yang, J., Yang, Y. S., Liu, Q. Q., Xu, G. F., and Cheng, X. N. (2010). Preparation of negative thermal expansion ZrW_2O_8 powders and its application in polyimide/ZrW_2O_8 composites. *J. Mater. Sci. Technol.* 26, 665–668. doi: 10.1016/S1005-0302(10)60103-X

Yang, X. B., Cheng, X. N., Yan, X. H., Yang, J., Fu, T. B., and Qiu, J. (2007). Synthesis of ZrO_2/ZrW_2O_8 composites with low thermal expansion. *Compos. Sci. Technol.* 67, 1167–1171. doi: 10.1016/j.compscitech.2006.05.012

Yilmaz, S. (2002). Thermal mismatch stress development in Cu-ZrW_2O_8 composite investigated by synchrotron X-ray diffraction. *Comp. Sci. Technol.* 62, 1835–1839. doi: 10.1016/S0266-3538(02)00104-5

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