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## High-temperature stability of nanozirconate-toughed IMF material lanthanum synthesized by an *in situ* reaction

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Herein, powders composed of  $\text{La}_2\text{Zr}_2\text{O}_7$  (LZ) and  $\text{ZrO}_2$  phases were synthesized by an *in situ* reaction using a sol-spray pyrolysis method; moreover, 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  (volume ratio = 1 : 1) powders were characterized by XRD, Raman spectroscopy, SEM, and TEM. XRD and Raman results showed that the samples maintained a tetragonal  $\text{ZrO}_2$  and a pyrochlore LZ phase from 900 to 1100 °C. The addition of LZ could be helpful in the stabilization of t- $\text{ZrO}_2$  and decreasing the grain size of  $\text{ZrO}_2$ . The SEM results revealed that the LZ and  $\text{ZrO}_2$  phases were homogeneously distributed in the sintered bulk. The HRTEM results suggested that the crystal orientations of the nano-LZ and nano- $\text{ZrO}_2$  phases were accordant; this was in agreement with the characteristics of the coherent boundaries. The fracture toughness of LZ- $\text{ZrO}_2$  was markedly improved by the transformation toughening of the  $\text{ZrO}_2$  phase, and a value that was 2.2-fold that of the LZ prepared by a similar technique was achieved.

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## 1. Introduction

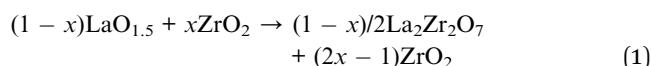
In inert matrix (IM) materials, plutonium is inlaid in a U-free matrix; hence, plutonium can be burnt without breeding any new plutonium by neutron capture in  $^{238}\text{U}$ . The basic criteria for IM materials are as follows: (i) stable irradiation behavior; (ii) good heat transport properties and phase stability at high working temperatures; and (iii) suitable mechanical properties such as elastic constants, fracture toughness and so on.<sup>1-4</sup>  $\text{La}_2\text{Zr}_2\text{O}_7$  (LZ) with a pyrochlore (P) structure is one of the most evaluated potential IM materials because of its good stable irradiation behavior and phase stability at high working temperatures.<sup>5,6</sup>

However, the low thermal conductivity and fracture toughness of LZ has limited its applications in a fuel cycle that relies on a reprocessing strategy. The use of higher-thermal-conductivity materials (such as  $\text{MgO}$  and  $\text{CeO}_2$ ) as a dual phase is a general method to improve the thermal conductivity of the IM materials.<sup>7,8</sup> However, only a few studies have been reported on the toughening of LZ. The incorporation of zirconia ( $\text{ZrO}_2$ ) with high toughness into alumina ceramics to deliberately toughen them has been widely carried out to achieve zirconia-toughened alumina (ZTA) systems.<sup>9,10</sup> Herein,  $\text{ZrO}_2$  has been incorporated into LZ to toughen it. Moreover,  $\text{ZrO}_2$  has a relatively high thermal conductivity with additional excellent radioactive resistance and good mechanical properties.<sup>11,12</sup> The tetragonal (t)-monoclinic (m) transition of zirconia is believed

to easily occur at temperatures less than 1150 °C.<sup>13</sup> This phase transition accompanying a change in the exterior environment induces a volume dilation of ~4 vol%. The stresses resulting from the volumetric changes can induce crack openings and thus limit the application of zirconia.<sup>14</sup>

Nanosized materials have relatively low activation energy for grain-boundary migration because of the increased surface (interface)/volume ratio as compared to their bulk counterparts.<sup>15,16</sup> For nanozirconia, when the crystallite size is ~30 nm or less, this phase transition occurs slowly. Moreover, nanocrystalline materials have a superior radiation resistance.<sup>17</sup>

The use of second-phase particles causes a grain-boundary motion by drag and can retard the grain growth of the matrix particles. It was reported that less than 1 mol%  $\text{LaO}_{1.5}$  could be dissolved in  $\text{ZrO}_2$ .<sup>18,19</sup> Based on the phase diagram of the  $\text{LaO}_{1.5}-\text{ZrO}_2$  system and the previous study, a pyrochlore-structured LZ phase exists in a wide concentration range of  $\text{LaO}_{1.5}$ . The phase composition of the  $x\text{LaO}_{1.5} - (1-x)\text{ZrO}_2$  ( $x \leq 1$ ) system at room temperature consists of LZ and  $\text{ZrO}_2$  with the following chemical formula:



Soft solution chemistry, such as a sol-gel method, has been used to fabricate lanthanum zirconate and yttria-stabilized zirconia.<sup>20</sup> It provides a possible route for the production of nanocrystalline LZ and nanocrystalline  $\text{ZrO}_2$  compounds in the nanometer scale. As a result, the grain size of  $\text{ZrO}_2$  or LZ in the composite will be smaller than that of the single-phase

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counterparts. It is suggested that the stabilization of t-ZrO<sub>2</sub> in the LaO<sub>1.5</sub>–ZrO<sub>2</sub> system may result from the impact of the LZ phase.

The objectives are to (i) prepare nano–nano LZ–ZrO<sub>2</sub> composite powders by an *in situ* reaction using a sol–spray pyrolysis method, (ii) measure the toughness of LZ–ZrO<sub>2</sub>, and (iii) study the high-temperature stability of LZ–ZrO<sub>2</sub>; this provides a method to toughen not only LZ, but also all other pyrochlore IM materials (such as Pu<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (ref. 21) and Nd<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> (ref. 8)); this will benefit the emerging area of IM research related to alternate ceramics.

## 2. Experimental procedures

### 2.1. Sample preparation

For the preparation of the LZ–ZrO<sub>2</sub> nanocomposite powders, 99.99% purity Zr(NO<sub>3</sub>)<sub>4</sub>·3H<sub>2</sub>O and La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Aladdin Chemistry Co., Ltd., Shanghai, China) were used as the starting materials and dissolved in deionized water; the concentration of Zr<sup>4+</sup> and La<sup>3+</sup> was 0.1 M. In the starting solution, citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>·H<sub>2</sub>O, 80 g L<sup>-1</sup>) and polyethylene glycol (PEG, molecular weight = 20 000, 50 g L<sup>-1</sup>) were used as the chelating agent and the plastering agent, respectively. The solution was stirred using a magnetic stirrer for 30 min to achieve complete dissolution. The resultant solution was then poured into a polytetrafluoroethylene (PTFE) tube and atomized by a stainless steel nozzle. Then, the precursors obtained from the sol–spray pyrolysis were annealed at 900–1200 °C for 6 h in high-purity Al<sub>2</sub>O<sub>3</sub> crucibles and cooled down to room temperature (heating and cooling rates = 2 °C min<sup>-1</sup>). To obtain dense samples, the powders were heated under an applied pressure of 40 MPa to 1450 °C at the constant heating rate of 100 min<sup>-1</sup> for 10 min and rapidly cooled down to room temperature. All the bulk samples prepared in this study had a diameter of 15 mm and a height of approximately 5 mm. The bulk samples were polished using a 0.025 µm diamond paste and thermally etched at 1200 °C for 10 h in air. The density of the samples was determined by the Archimedes method.

### 2.2. Characterization of the sample composition and microstructure

X-ray diffraction (XRD) analysis of the samples was carried out using the X’Pert PRO diffractometer with Cu K $\alpha$  radiation ( $\lambda$  = 0.15406 nm; PANalytical, Almelo, the Netherlands). The XRD patterns were obtained in the  $2\theta$  range of 10–90° at room temperature at the scanning rate of 0.05° s<sup>-1</sup> and a step size of 0.033°. The crystallite size was calculated using the Scherrer’s formula for the 440, 220 and 111 peaks of La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub>, t-ZrO<sub>2</sub>, and m-ZrO<sub>2</sub>, respectively:

$$D = \frac{0.89\lambda}{(\beta_{\text{obs}} - \beta_{\text{std}})\cos\theta} \quad (2)$$

where  $D$  is the crystallite size (nm),  $\lambda$  is the wavelength (nm),  $\beta_{\text{obs}}$  is the FWHM,  $\beta_{\text{std}}$  is the instrumental broadening parameters (0.05°), and  $\theta$  is the diffraction angle.

Raman spectra were obtained using the Renishaw InVia Raman spectrometer (Renishaw plc, New Mills, UK). The emission line at 514.5 nm obtained from an Ar<sup>+</sup> ion laser was used as the excitation source. The samples of the bulk were observed using a field emission scanning electron microscope (FESEM, Apollo 300 FE, Onducat CamScan Ltd., Cambridge, UK) operated at 30 kV. The TEM observation of the samples was conducted using a transmission electron microscope (TEM, JEM-2010, JEOL, Tokyo, Japan).

### 2.3. Characterization of the sample fracture toughness

A Vickers hardness tester (HV-1000A, Huayin Test Instrument Co., Ltd., Yantai, China) was used to measure the indentation fracture toughness. The indentations were made on polished surfaces with a load ( $F$ ) of 9.8 N held for 10 s. The fracture toughness ( $K_{\text{IC}}$ , MPa m<sup>1/2</sup>) for each sample was estimated from a minimum of 9 indents to reduce the experimental uncertainty using the following equation:<sup>22,23</sup>

$$K_{\text{IC}} = 0.16 \times H_V \times a^{1/2} \times \left(\frac{c}{a}\right)^{-3/2} \quad (c/a \geq 2.5) \quad (3)$$

where  $H_V$  is the hardness,  $a$  is half the diagonal length of the Vickers indent (µm), and  $c$  is the crack length measured from the indent center (µm). The values of  $a$  and  $c$  were measured using an SEM instrument.

## 3. Results and discussion

### 3.1. Characterization of the LZ–ZrO<sub>2</sub> powders

X-ray diffraction was employed to investigate the crystalline phases of lanthanum zirconate and zirconia. The XRD patterns of  $x\text{LaO}_{1.5} - (1-x)\text{ZrO}_2$  ( $x = 0\text{--}0.5$ ) powders obtained after annealing the powders at 1200 °C for 6 h are shown in Fig. 1. In the pattern of pure ZrO<sub>2</sub>, no clear evidence is found for the presence of the t and c peaks. The shifts of the (–111) and (111) peaks in the pattern of 1 mol% LaO<sub>1.5</sub>–ZrO<sub>2</sub> are an indication

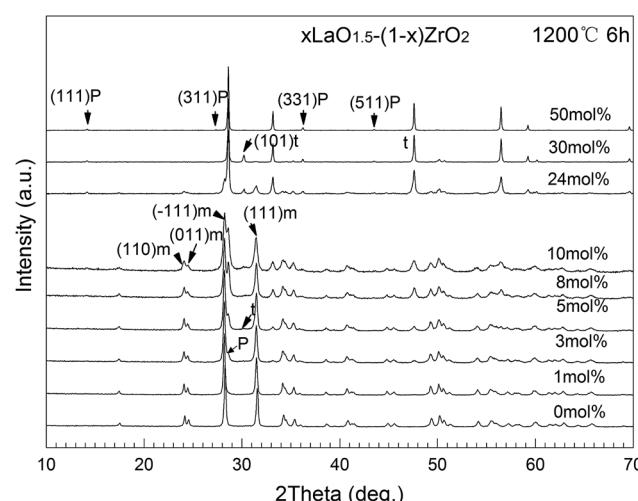


Fig. 1 XRD patterns of the  $x\text{LaO}_{1.5} - (1-x)\text{ZrO}_2$  ( $x = 0\text{--}50$  mol%) powders after annealing at 1200 °C for 6 h in air.



that  $\text{LaO}_{1.5}$  has been completely doped into the  $\text{ZrO}_2$  crystal by substituting  $\text{La}^{3+}$  for  $\text{Zr}^{4+}$ . The presence of the pyrochlore structure is confirmed by the occurrence of the superlattice 311, 331, and 511 peaks.<sup>24</sup> The results indicate that the solubility of  $\text{LaO}_{1.5}$  in  $\text{ZrO}_2$  is lower than 1 mol%; this is in line with that reported in literature.<sup>18,19</sup> The broadening of the m (111) peaks indicated that the grain size of m- $\text{ZrO}_2$  decreased with an increase in the content of LZ. Considering the grain size effect of  $\text{ZrO}_2$ , the presence of the (101) peak for t- $\text{ZrO}_2$  could be attributed to the grain refinement.

Table 1 summarizes the calculated grain sizes of m- $\text{ZrO}_2$  in  $x\text{LaO}_{1.5} - (1-x)\text{ZrO}_2$  ( $x = 0-0.4$ ) powders after annealing at 1200 °C for 6 h. The data showed that the grain size of the m phase gradually decreased with the increasing concentration of  $\text{LaO}_{1.5}$ , reaching a value that was approximately equal to the critical grain size of t- to m- $\text{ZrO}_2$  at the addition concentration of 10 and 24 mol%. The (101) peak for t- $\text{ZrO}_2$  significantly increased at the concentration of 24 mol%. The lattice parameters of LZ and  $\text{ZrO}_2$  were determined based on the XRD patterns shown in Fig. 1. The volume ratios of LZ and m- $\text{ZrO}_2$  in the samples could be easily calculated using the weight and the number of formula units per elementary cell, which were approximately 1/4, 1/1 and 4/1 for 10, 24 and 40 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  samples, respectively. The 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  powders were chosen for further characterization.

### 3.2. Fracture toughness

Fig. 2(a) shows the fracture surface of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  spark plasma sintered (SPS) bulk sample after thermal etching at 1100 °C for 2 h. The SEM image reveals that the particle size of the SPS bulk sample is in the range of 50–200 nm. The SEM image reveals that the sintered sample has a dense microstructure, which is very important for the mechanics performance testing. The densities of the sintered LZ and 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  specimens were determined by the Archimedes method to be 97.6% and 95.8% of the theoretical values, respectively.

Fig. 2(b) shows the fracture toughness of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  sample, and the data have been compared with that of the LZ materials. The experimental results for the LZ

**Table 1** The calculated crystallite sizes and phase composition of m- $\text{ZrO}_2$  in  $x\text{LaO}_{1.5} - (1-x)\text{ZrO}_2$  ( $x = 0-0.4$ ) powders after annealing at 1200 °C for 6 h<sup>a</sup>

LaO <sub>1.5</sub> concentration (mol%)	Phase composition	Crystallite size of m- $\text{ZrO}_2$ (nm)
0	m	38.8
1	m	40.1
3	m + P	32.6
5	m + P + t*	31.0
8	m + P + t*	28.1
10	m + P + t*	22.5
24	P + m + t	23.4
40	P + t + m*	—

<sup>a</sup> P – pyrochlore-type  $\text{La}_2\text{Zr}_2\text{O}_7$ ; m – m- $\text{ZrO}_2$ ; t – t- $\text{ZrO}_2$ ; \*small amount.

samples are in good agreement with those reported in the literature.<sup>25</sup> The data showed that the toughness level of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  was 120% greater than that of LZ ( $\sim 1.0 \text{ MP m}^{1/2}$ ). The high fracture toughness of 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  (as compared to that of LZ) can be attributed to the transformation toughening from the martensitic transformation of the t to the m phases.

### 3.3. High-temperature stability and grain growth

Fig. 3 shows the XRD patterns of  $\text{ZrO}_2$  and 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  powders after annealing at 500–1100 °C. Pure  $\text{ZrO}_2$  presents clear t peaks at 500 °C. With an increase in the annealing temperature from 600 to 800 °C, pure  $\text{ZrO}_2$  undergoes a t to m phase transformation. The grain size of the t phase was below 30 nm (see Table 2), in good agreement with the critical grain size for the t- to m- $\text{ZrO}_2$  transformation.<sup>26</sup> Compared with the case of pure  $\text{ZrO}_2$ , no clear evidence was found for the shift of the t (101) peaks in any of the patterns of 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$ ; this indicated that the solubility of  $\text{La}^{3+}$  in the  $\text{ZrO}_2$  phase was negligible. Table 2 lists the grain sizes of  $\text{ZrO}_2$  and 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  powders calculated from the Scherrer's formula on the basis of Fig. 3. For pure  $\text{ZrO}_2$ , the crystallite size of t- $\text{ZrO}_2$  increased from 9.1 to 26.4 nm as the temperature was increased from 500 to 800 °C, and t- $\text{ZrO}_2$  disappeared above 900 °C. The crystallite sizes of LZ and  $\text{ZrO}_2$  in the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  system gradually increased from 19.5 to 38.1 nm and from 8.7 to 38.5 nm as the annealing temperature was elevated from 900 to 1100 °C. When the addition concentration of  $\text{LaO}_{1.5}$  reached 24 mol%, the critical grain size for the t to m phase transformation increased from  $\sim 20$  to  $\sim 40$  nm when the corresponding heat treatment temperature was increased from 600 to 1100 °C. The data showed that the addition of LZ could be helpful in decreasing the grain size of  $\text{ZrO}_2$ .

Raman spectroscopy is another useful technique that is generally used to investigate the structures of lanthanum zirconate and zirconia. Fig. 4 shows the Raman spectra of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  powders annealed at 800, 900, and 1100 °C and the P-LZ samples.<sup>27</sup> The bands at 298, 389, 494, 511, and 744  $\text{cm}^{-1}$  were assigned to the  $\text{A}_{1g} + \text{E}_g + 4\text{F}_{2g}$  Raman active vibration modes (gray arrows) of the P-LZ sample. The bands corresponding to the  $\text{A}_{1g} + 3\text{E}_g$  modes (black arrows) of t- $\text{ZrO}_2$  were clearly observed at 273, 463, 600 and 646  $\text{cm}^{-1}$  in the spectra of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  powders,<sup>28</sup> in good agreement with the XRD results.

Fig. 5(a) and 4(b) show the SEM images of the 24 mol%  $\text{LaO}_{1.5}$ - $\text{ZrO}_2$  bulk samples after sintering at 1300 °C for 48 h at different magnifications. Fig. 5(a) reveals that the samples have a homogeneous microstructure. The particle size distribution of the samples is shown in Fig. 5(c), and the observed grain size of the samples is in the range of 0.1–1.4  $\mu\text{m}$ . Fig. 5(b) reveals that the crystal grains of the sample are near spheroidal in shape. The SEM image also shows that the grains of the sample are closely bonded with each other, and the interfaces between grains are legible. In a previous study on the nano–nano composites of lanthanum zirconate and yttria-stabilized zirconia,<sup>20</sup> the activation energy for the grain growth of LZ



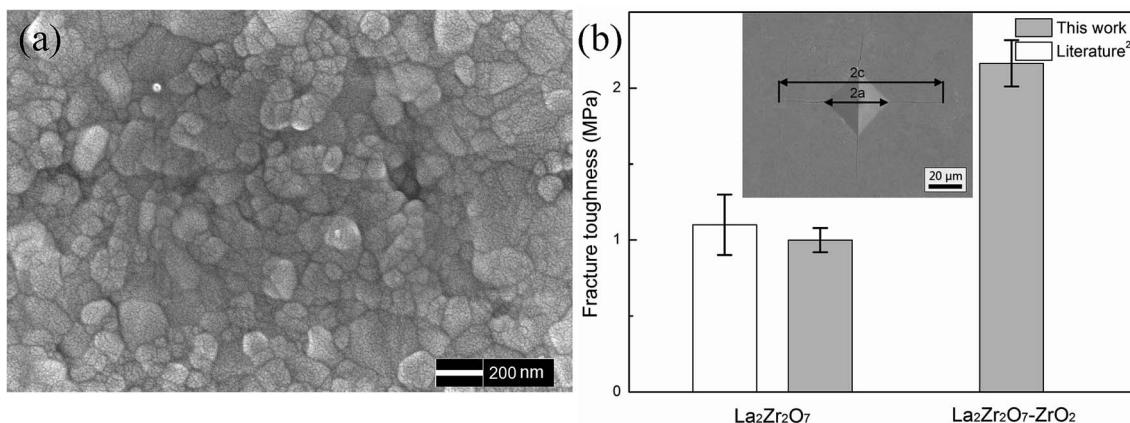


Fig. 2 (a) The SEM image of the 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  bulk sample. (b) Fracture toughness of the 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  and  $\text{La}_2\text{Zr}_2\text{O}_7$  bulk samples. The data for  $\text{La}_2\text{Zr}_2\text{O}_7$  is obtained from the study reported by Vassen *et al.*<sup>25</sup> Inset shows a Vickers indentation with cracks (polished, SEM, SE) by a 1 kg load of 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  ceramics.

$(225 \pm 12 \text{ kJ mol}^{-1})$  was much lower than that of 10YSZ (yttria-stabilized zirconia,  $382 \pm 17 \text{ kJ mol}^{-1}$ ); this suggested that the first step was the formation of LZ and nuclei, and then,  $\text{ZrO}_2$  nucleated on the surface of the LZ crystalline grains during the annealing process. Therefore, the small crystals were the  $\text{ZrO}_2$  nuclei, which were evenly distributed on the surface of the LZ nuclei *via* encircling and insertion.

To rationalize these results, the phase transformation mechanism of  $\text{ZrO}_2$  was considered. Pure zirconia has three polymorphs under ordinary pressure, and the monoclinic type is the most frequent structure at room temperature and up to  $1170^\circ\text{C}$ . In our case, pure  $\text{ZrO}_2$  and  $\text{ZrO}_2$  coexisting in the composite powders possess the t phase at  $500^\circ\text{C}$  and  $800-1100^\circ\text{C}$ , as confirmed by the XRD measurements. The appearance of the high-temperature phase at low temperatures has been discussed, and Parija *et al.*<sup>29</sup> have proposed that the main reason for the stabilization is the crystallite size effect. According to their opinion, the following equation for the radius of the critical crystallite size  $r_c$  for the t-m transformation has been proposed:

$$r_c = -3\Delta\sigma/[q(1 - T/T_b) + \Delta\epsilon] \quad (4)$$

where  $\Delta\epsilon$  is the change in the strain energy/unit volume for a particle,  $q$  is the heat of the t-m transformation,  $\Delta\sigma$  is the difference between the surface-free energies of the m and t phases of  $\text{ZrO}_2$ ,  $T_b$  is the temperature at which the t-m transformation occurs for  $\text{ZrO}_2$  ( $1170^\circ\text{C}$ ), and  $T$  is the temperature at which the crystallites of a given radius  $r_c$  undergo the t-m transformation. At room temperature, the following parameter values were used for the calculation of  $r_c$ :  $\Delta\sigma = 0.91 \text{ J m}^{-2}$ ,  $q =$

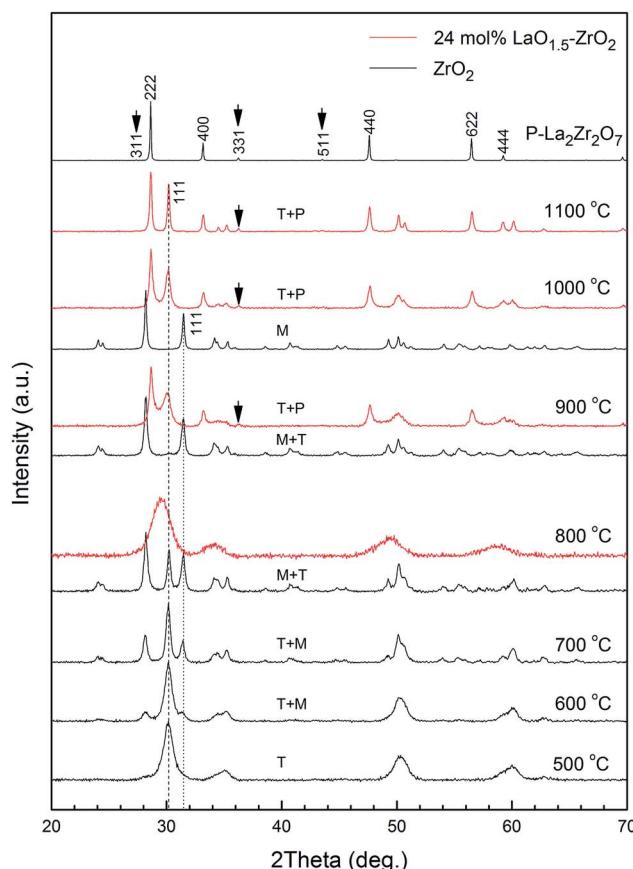


Fig. 3 XRD patterns of  $\text{ZrO}_2$  and 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  powders after annealing at  $500-1100^\circ\text{C}$  for 6 h.

Table 2 The calculated crystallite sizes for  $\text{ZrO}_2$  and 24 mol%  $\text{LaO}_{1.5}-\text{ZrO}_2$  after annealing at  $500-1100^\circ\text{C}$  for 6 h

Sample ( $^\circ\text{C}$ )	Crystallite size (nm)			
	$\text{ZrO}_2$	24 mol% $\text{LaO}_{1.5}-\text{ZrO}_2$	t	m
500	9.1	—	—	—
600	11.2	—	—	—
700	21.3	24.9	—	—
800	26.4	24.8	—	—
900	—	29.9	8.7	19.5
1000	—	42.9	16.9	24.1
1100	—	—	38.5	38.1



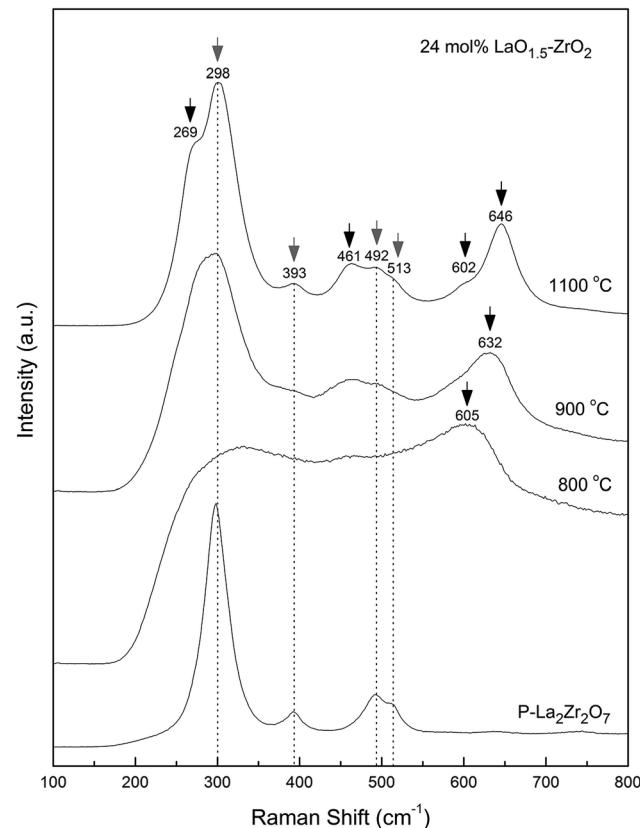


Fig. 4 Raman spectra of 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  powders after annealing at 800, 900, and 1100 °C for 6 h, and  $\text{La}_2\text{Zr}_2\text{O}_7$ .

$-2.82 \times 10^8 \text{ J m}^{-1}$ ,<sup>3</sup>  $T_b = 1443 \text{ K}$ ,  $T = 298 \text{ K}$ , and  $\Delta\epsilon = 0.46 \times 10^8 \text{ J m}^{-1}$ .<sup>3</sup> The value of  $r_c$  is *ca.* 15 nm.

The grain size of pure  $\text{ZrO}_2$  presented in Table 1 corresponds well with the calculated  $r_c$ . Similar to that of 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$ , the t- $\text{ZrO}_2$  phase is stable even at the grain size of 38.5 nm. As indicated in eqn (3), the value of  $r_c$  depends on  $\Delta\sigma$ ,  $q$ ,  $T_b$ ,  $T$ , and  $\Delta\epsilon$ . In Fig. 2, no peak shift of the t and m phases was observed for all the samples; this indicated that La was not doped into the  $\text{ZrO}_2$  crystal. This suggests that the values of  $\Delta\sigma$  and  $q$  are consistent with those of pure  $\text{ZrO}_2$ .  $T_b$  and  $T$  are constant; thus, the change in the strain energy may be the main factor for the increased  $r_c$ .

In the Raman spectra (Fig. 4), a significant shift ( $\sim 14 \text{ cm}^{-1}$ ) towards lower frequencies for t- $\text{ZrO}_2$  was observed in the range of 600–650  $\text{cm}^{-1}$  with a decrease in the annealing temperature from 1100 to 900 °C. Djurado *et al.*<sup>26</sup> reported that the grain size effect on the Raman spectra was much smaller than the pressure-induced effect, and the maximum shift value was less than 10  $\text{cm}^{-1}$ . This suggests that stress exists in the  $\text{LaO}_{1.5}\text{-ZrO}_2$  composite samples. Furthermore, the SEM images (Fig. 5(b)) show that small  $\text{ZrO}_2$  particles are embedded into the large LZ particles. In other words, the  $\text{ZrO}_2$  particles grew at the grain boundary.

To confirm the grain-boundary growth, high-resolution TEM characterization was performed. Fig. 6 shows a TEM image of the 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  powders after annealing at 1000 °C for 6 h. The lattice fringes with 0.620 and 0.315 nm spacings can be assigned to the 111 lattice plane of pyrochlore-LZ (P-LZ) and

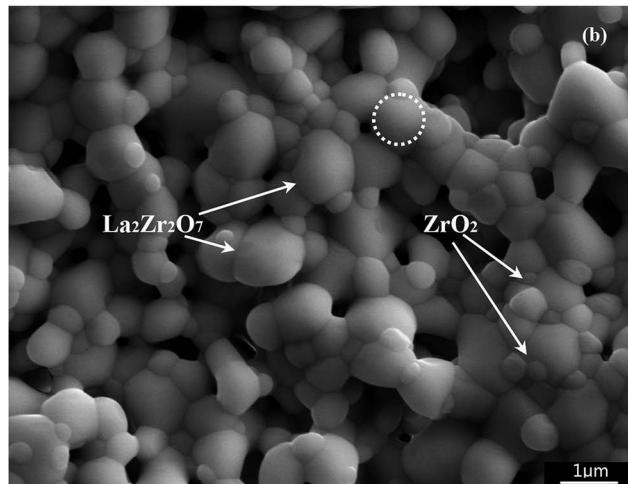
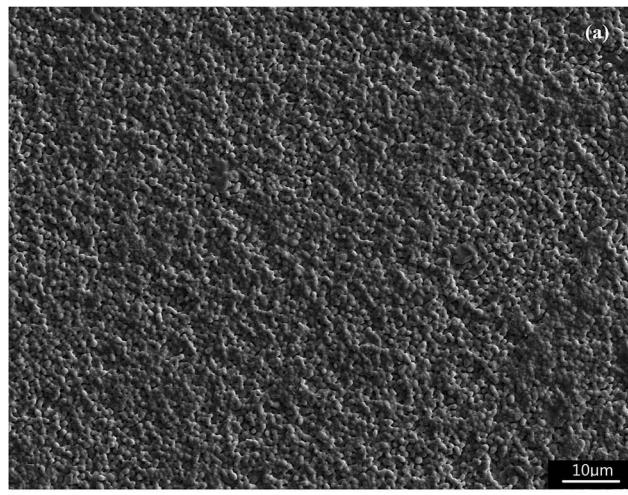


Fig. 5 (a) and (b) SEM images of 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  bulk samples after sintering at 1300 °C for 48 h, and (c) particle size distribution of the 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  bulk sample obtained from the SEM images.

the 111 lattice plane of t- $\text{ZrO}_2$  phase, respectively. The TEM image shows that the  $\text{ZrO}_2$  crystal grows along the surface of the LZ crystal, and the crystal orientation of the two phases is accordant, in line with the characteristics of coherent boundaries. The coherent boundaries with low excess energies are

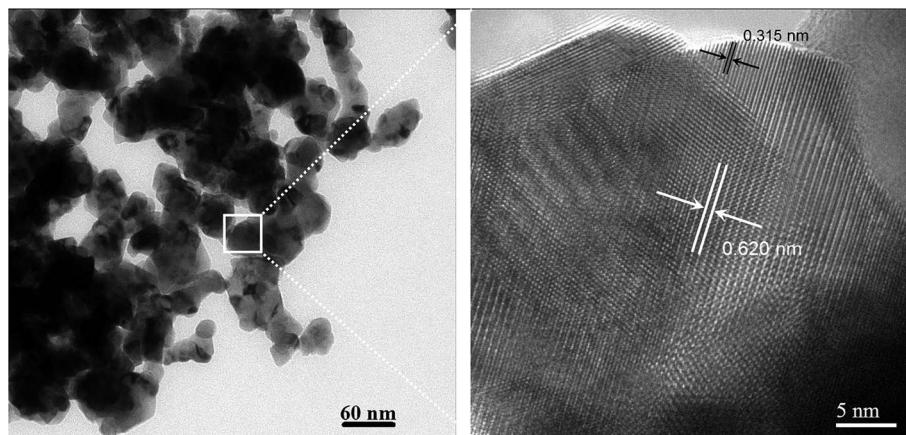


Fig. 6 TEM images of 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  powders after annealing at 1000 °C for 6 h.

believed to retard the grain growth of the matrix particles because the grain growth of nanosized materials is controlled by the grain-boundary migration. Hence, the stabilization mechanism of the  $\text{t-ZrO}_2$  phase of the LZ- $\text{ZrO}_2$  composite powders should be attributed to the grain refinement and lattice stress effects.

Based on the abovementioned analysis, the lowest entropy will be selected during the *in situ* reaction. A possible mechanism for the formation of the  $\text{LaO}_{1.5}\text{-ZrO}_2$  nano-nano composite powders has been suggested as follows: the first step is the formation of LZ and nuclei, and then,  $\text{ZrO}_2$  nucleates on the surface of LZ crystalline grains during the annealing process.

## 4. Conclusions

In summary, the addition of  $\text{LaO}_{1.5}$  to  $\text{ZrO}_2$  forms a pyrochlore structural  $\text{La}_2\text{Zr}_2\text{O}_7$  phase and induces a tetragonal to monoclinic (t to m) phase transition of  $\text{ZrO}_2$ . The addition of LZ could be helpful in stabilizing  $\text{t-ZrO}_2$  and decreasing the grain size of  $\text{ZrO}_2$ . The  $\text{t-ZrO}_2$  phase in the 24 mol%  $\text{LaO}_{1.5}\text{-ZrO}_2$  powders was phase-stable up to a calcination temperature of 1100 °C. Since the solubility of  $\text{LaO}_{1.5}$  in  $\text{ZrO}_2$  is lower than 1 mol%, the presence of the  $\text{t-ZrO}_2$  phase in the  $\text{LaO}_{1.5}\text{-ZrO}_2$  system does not arise from doping stabilization by the substitution of  $\text{La}^{3+}$  for  $\text{Zr}^{4+}$ , but rather from the grain refinement of the LZ phase. The crystal orientation of the nano-LZ and nano- $\text{ZrO}_2$  phases was accordant, in line with the characteristics of the coherent boundaries. The fracture toughness of  $\text{La}_2\text{Zr}_2\text{O}_7\text{-ZrO}_2$  has been markedly improved by the transformation toughening of the  $\text{ZrO}_2$  phase, reaching a value that is 2.2-fold that of  $\text{La}_2\text{Zr}_2\text{O}_7$  prepared by a similar technique.

## Conflicts of interest

There are no conflicts to declare.

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## References

- 1 H. Matzke, V. V. Rondinella and T. Wiss, *J. Nucl. Mater.*, 1999, **274**, 47–53.
- 2 C. Degueldre and J. M. Paratte, *J. Nucl. Mater.*, 1999, **274**, 1–6.
- 3 S. Lutique, D. Staicu, R. J. M. Konings, V. V. Rondinella, J. Somers and T. Wiss, *J. Nucl. Mater.*, 2003, **319**, 59–64.
- 4 R. Restani, M. Martin, N. Kivel and D. Gavillet, *J. Nucl. Mater.*, 2009, **385**, 435–442.
- 5 I. Hayakawa and H. Kamizono, *J. Nucl. Mater.*, 1993, **202**, 163–168.
- 6 S. Yamazaki, T. Yamashita, T. Matsui and T. Nagasaki, *J. Nucl. Mater.*, 2001, **294**, 183–187.
- 7 A. Imaura, N. Touran and R. C. Ewing, *J. Nucl. Mater.*, 2009, **389**, 341–350.
- 8 A. T. Nelson, M. M. Giachino, J. C. Nino and K. J. McClellan, *J. Nucl. Mater.*, 2014, **444**, 385–392.
- 9 N. Claussen, *J. Am. Ceram. Soc.*, 1976, **59**, 49–51.
- 10 D. J. Green, *J. Am. Ceram. Soc.*, 1982, **65**, 610–614.
- 11 C. Degueldre, T. Arima and Y. W. Lee, *J. Nucl. Mater.*, 2003, **319**, 6–14.
- 12 C. Ghosh, S. Sinhamahapatra and H. S. Tripathi, *Int. J. Appl. Ceram. Technol.*, 2018, **00**, 1–8.
- 13 R. Chaim, D. G. Brandon and A. H. Heuer, *Acta Metall.*, 1986, **34**, 1933–1939.
- 14 D. R. Clarke and C. G. Levi, *Annu. Rev. Mater. Res.*, 2003, **33**, 383–417.
- 15 W. P. Tong, N. R. Tao, Z. B. Wang, J. Lu and K. Lu, *Science*, 2003, **299**, 686–688.
- 16 K. Dick, T. Dhanasekaran, Z. Zhang and D. Meisel, *J. Am. Chem. Soc.*, 2002, **124**, 2312–2317.
- 17 S. Wurster and R. Pippan, *Scr. Mater.*, 2009, **60**, 1083–1087.
- 18 B. Bastide, P. Odier and J. P. Coutures, *J. Am. Ceram. Soc.*, 1988, **71**, 449–453.



19 M. A. Stough and J. R. Hellmann, *J. Am. Ceram. Soc.*, 2002, **85**, 2895–2902.

20 K. Jiang, S. Liu and C. Li, *J. Am. Ceram. Soc.*, 2013, **96**, 3296–3303.

21 R. Chawla, P. Grimm, P. Heimgartner, F. Jatuff, G. Ledegerber, A. Luthi, M. Murphy, R. Seiler and R. van Geemert, *Prog. Nucl. Energy*, 2001, **38**, 359–362.

22 A. G. Evans and E. A. Charles, *J. Am. Ceram. Soc.*, 1976, **59**, 371–372.

23 G. R. Anstis, P. Chantikul, B. R. Lawn and D. B. Marshall, *J. Am. Ceram. Soc.*, 1981, **64**, 533–538.

24 P. K. Schelling and S. R. Phillipot, *J. Am. Ceram. Soc.*, 2001, **84**, 2997–3007.

25 R. Vassen, X. Cao, F. Tietz, D. Basu and D. Stöver, *J. Am. Ceram. Soc.*, 2000, **83**, 2023–2028.

26 E. Djurado, P. Bouvier and G. Lucaleau, *J. Solid State Chem.*, 2000, **149**, 399–407.

27 D. Michel, M. P. y. Jorba and R. Collongues, *J. Raman Spectrosc.*, 1976, **5**, 163–180.

28 P. Bouvier and G. Lucaleau, *J. Phys. Chem. Solids*, 2000, **61**, 569–578.

29 A. Parija, G. R. Waetzig, J. L. Andrews and S. Banerjee, *J. Phys. Chem. C*, 2018, **122**, 25709–25728.

