Molten Salt Synthesis of $\text{La}_2\text{Zr}_2\text{O}_7$ Ultrafine Powders

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Abstract:

Ultrafine powders of pyrochlore-type $\text{La}_2\text{Zr}_2\text{O}_7$ were synthesized via a simple molten salt mediated process using zirconium oxide and lanthanum oxide as raw materials, and sodium chloride, potassium chloride and sodium fluoride to form a reaction medium. The effects of reaction temperature, salt/reactant ratio and salt type on the $\text{La}_2\text{Zr}_2\text{O}_7$ formation were investigated. Among the three attempted salt assemblies (KCl–LiCl, Na_2CO_3 – K_2CO_3 , and NaCl–KCl–NaF), NaCl–KCl–NaF showed the best accelerating effect on the $\text{La}_2\text{Zr}_2\text{O}_7$ formation. At a given temperature, the $\text{La}_2\text{Zr}_2\text{O}_7$ content in the final products increased with the increase in the salt amount. Phase pure submicron sized $\text{La}_2\text{Zr}_2\text{O}_7$ ultrafine powders were obtained after 3h firing at 1100°C with the salt/reactant weight ratio of 5:1 or at 1200 °C with salt/reactant weight ratio of 3:1. The synthesis temperature (1100 °C) was much lower than that required by the conventional solid–state mixing method or a wet chemical method. The “dissolution–precipitation” mechanism had dominated the synthesis process.

Key words: $\text{La}_2\text{Zr}_2\text{O}_7$; Molten salt; Ultrafine powders.

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1 Introduction

Pyrochlore-type lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$, LZO) is an important rare earth zirconate for structural and functional applications owing to its high melting point (2300 °C), low thermal conductivity ($1.56 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ at 1000 °C), excellent thermal stability, as well as high tolerance to defects and ultraviolet absorption [1–3]. Homogeneous LZO particles with a high crystallinity and high purity, in particular, have attracted much attention in recent years and been used for thermal barrier coatings (TBCs) of engine turbines, hosts for radioactive waste and surplus actinides, and photocatalysts for dye degradation [4–7].

Several techniques have been applied to prepare LZO powders, including the conventional solid-state mixing method (CSSM) [8, 9], co-precipitation synthesis [10, 11], hydrothermal synthesis [12], combustion synthesis [13], sol-gel synthesis [5, 14], and molten salt synthesis (MSS) [15, 16]. In the case of MSS, reactants can partially dissolve in the molten salt medium, facilitating the mixing and diffusion of reactant species and thus the subsequent reaction at a relatively low temperature. In addition, the synthesis generally can be carried out under mild conditions without using specialty reaction vessels and expensive raw materials. Mao et al. [15] synthesized LZO nanopowders via MSS at a low temperature. Although expensive zirconyl chloride octahydrate and lanthanum nitrate were used as the starting raw materials and a complex co-precipitation process

was used to prepare the precursors for the MSS, fluorite-type rather than pyrochlore-type LZO was obtained. By changing the salt assembly, Wang et al. [16] prepared pyrochlore-type LZO nanopowders at 900 °C. Unfortunately, the product powders had a low crystallinity and poor chemical purity. In addition, the combined co-precipitation and MSS process used in both studies was difficult to operate and of high cost. Therefore, it is necessary to develop an improved MSS process which can overcome the disadvantages mentioned above and be used to synthesize pure pyrochlore-type LZO ultrafine particles with a high crystallinity.

In response to this, in this work, a more straightforward MSS route was investigated and used to synthesize high quality LZO ultrafine powders directly from relatively cheaper zirconium oxide and lanthanum oxide raw materials. The effects of temperature, salt/reactant ratio and salt type on the synthesis process were investigated and discussed, based on which the relevant reaction mechanisms proposed.

2 Experimental

2.1 Raw materials and sample preparation

ZrO₂ (99.0%; Guoyao Chem. Co. Ltd., Shanghai, China) and La₂O₃ (99.9%; Shanpu Chem. Co. Ltd., Shanghai, China) were used as raw materials and NaCl (99.5%; Bodi Chem. Co. Ltd., Tianjing, China), KCl (99.5%; Bodi Chem. Co. Ltd., Tianjing, China), NaF (98.0%; Yongda Chem. Co. Ltd., Tianjing, China), LiCl ·H₂O (97.0%, Guoyao Chem. Co. Ltd., Shanghai, China), Na₂CO₃(99.8%; Bodi Chem. Co. Ltd., Tianjing, China) and K₂CO₃ (99.0%; Bodi Chem. Co. Ltd., Tianjing, China) used to form molten salt media.

ZrO₂ and La₂O₃ powders mixed in the molar ratio of 2:1 were combined with various amounts of salts in an agate mortar, and placed in a corundum crucible before being heated at 900–1200 °C for 3 h in a muffle furnace. After heating and subsequent cooling to room temperature, the reacted masses were washed repeatedly with distilled water to remove the residual salt. The resultant product powders were oven-dried overnight at 80 °C for further characterization. Batch compositions of samples and their firing conditions are listed in Table 1.

2.2 Sample characterization

Phases in samples were identified by means of powder X-ray diffraction (XRD) analysis using a Philips X'Pert PRO diffractometer (PANalytical, NETHERLANDS). Spectra within the range between 10° and 90° (2θ) were recorded at 40 mA and 40 kV using Cu K_α radiation (λ = 0.1542 nm). ICDD cards, No. 73-0444, 78-0047, 74-2430, 75-1900, 89-6883 and 89-5168 were used for the identification of LZO, ZrO₂, La₂O₃, La(OH)₃, LaOCl and LaOF, respectively. Relative contents of crystalline phases in the samples were calculated by using the Rietveld refinement method [17, 18].

Microstructures and morphologies of the samples were examined using a field emission gun scanning electron microscope (FE-SEM, Nova400NanoSEM, PHILIPS, NETHERLANDS, 15 kV) and a transmission electron microscope (TEM, JEM-2100UHRSTEM, JEOL, JAPAN, 200 kV). Samples for the former were coated with gold and for the latter prepared by 2 h ultrasonic dispersion in ethanol, followed by dropping and drying the suspension onto a holey carbon film. Selected area electron diffraction (SAED), along with energy-dispersive spectroscopy (EDS), was used for assisting phase identification.

3 Results and Discussion

3.1 Effect of salt type on the LZO formation

Fig. 1 demonstrates the effects of salt type on the reaction extents in samples (S1, S2 and S3) after 3 h at 1100°C (with salt/reactant weight ratio of 5:1). When KCl–LiCl was used, LZO and LaOCl were formed as the main crystalline phases, along with some residual ZrO_2 . When Na_2CO_3 – K_2CO_3 was used, LZO became the primary phase whereas small amounts of ZrO_2 and La_2O_3 (indicated by $\text{La}(\text{OH})_3$ which was from the hydration of La_2O_3) still remained. However, when NaCl–KCl–NaF was used, only LZO was detected. Fig. 2 further gives relative contents of crystalline phases in the samples mentioned above. 58 and 73 wt% LZO were formed when KCl–LiCl and Na_2CO_3 – K_2CO_3 were respectively used. In the case of using NaCl–KCl–NaF, however, the LZO content reached 100wt%. These results indicated that NaCl–KCl–NaF had the best accelerating effect on the LZO formation, which could be attributed to the higher solubility of ZrO_2 and La_2O_3 and more rapid diffusion and reaction in it than in the other two binary salts [19].

3.2 Effect of heating temperature on the LZO formation

Fig. 3 shows XRD patterns of samples (T1, T2, T3 and T4) after 3 h firing at 900–1200 °C (with the salt/reactant weight ratio of 3:1). At 900 °C, some LZO was already formed but ZrO_2 and La_2O_3 still remained as the main phases, indicating that the low extents of reaction at this temperature. In addition, LaOF was formed as an intermediate phase (see Section 3.5 below). At 1000 °C, the LZO peaks height increased. Although La_2O_3 disappeared, ZrO_2 and LaOF still remained. On increasing the temperature to 1100 °C, LZO became the main crystalline phase and ZrO_2 and LaOF decreased evidently. Finally, upon further increasing the temperature to 1200 °C, apart from LZO, no other phases were detected, indicating that the formation of LZO had been completed and phase pure LZO

was obtained.

Presented in Fig. 4 are relative contents of crystalline phases in the samples whose XRD are shown in Fig. 3. At 900 °C, there was only about 27 wt% LZO in the sample, along with respectively 40, 14 and 19 wt% of ZrO_2 , LaOF and La_2O_3 . On increasing the temperature to 1000 °C, LZO increased to 40 wt%. Upon further increasing the temperature to 1100 °C, LZO increased to 67 wt%, but 13 wt% ZrO_2 and 20 wt% LaOF still remained in the sample. Finally, after firing at 1200 °C, the content of LZO reached 100 wt%. These results further confirmed that phase pure LZO powders were prepared after 3 h at 1200 °C with the salt/reactant weight ratio of 3:1.

3.3 Effect of salt content on the LZO formation

Fig. 5 shows XRD patterns of samples (RS0, RS1, T3 and RS3) after 3h firing at 1100 °C with different salt/reactant weight ratios. When the salt was absent, ZrO_2 and La_2O_3 were detected as the main phases, and only minor LZO was formed, indicating low extents of the formation reaction. However, when NaCl–KCl–NaF was used, the extents of the formation reaction increased evidently. When the salt/reactant weight ratio was 1:1, LZO was formed as the main phase, along with only small amounts of LaOF and ZrO_2 . Furthermore, no La_2O_3 was detected. On increasing the ratio to 3:1, LZO peaks became higher, and on further increasing the ratio to 5:1, only LZO phase was detected, indicating the formation of phase pure LZO. These results indicated that it was necessary to use appropriately high amounts of molten salt to accelerate the LZO formation and phase pure LZO could be synthesized at 1100 °C with the salt/reactant weight ratio of 5:1. This synthesis temperature was much lower than required by CSSM (over 1500 °C) [8, 9] and most of the wet–chemical techniques [5, 11, 14]. For example, Wang et al. [5], Chen et al. [11] and Kong et al. [14] synthesized LZO nanopowders with various sizes at 1200 °C, from precursors derived from a sol–gel and/or

co-precipitation process. Based on these, it can be concluded that, compared to the sol-gel or co-precipitation method, the present MSS method not only lowered the synthesis temperature of LZO powders, but also simplified/shortened the overall preparation process.

Fig. 6 further illustrates the effects of salt content on the relative contents of crystalline phases in the samples whose XRD patterns are shown in Fig. 5. The LZO content increased with increasing the salt to reactant ratio. When no salt was used, the LZO content was only 27 wt%. When the salt/reactant ratio was 1:1, the LZO content increased to 51 wt%. Upon increasing the salt/reactant ratio to 3:1, it further increased to 67 wt%. And finally upon further increasing the ratio to 5:1, it reached 100 wt%. The higher yield of LZO with salt content increasing can be attributed to that higher salt content is more beneficial for the dissolution of raw La_2O_3 and ZrO_2 in NaCl-KCl-NaF , and the higher concentration of the reactants then results in a higher formation rate of LZO [20, 21]. These results indicated that the optimal salt/reactant weight ratio for the present molten salt process was 5:1.

3.4 Microstructure of as-prepared LZO powders

Presented in Fig. 7 are FE-SEM images of the product powders prepared in NaCl-KCl-NaF . In the sample prepared at 1100 °C with the salt/reactant ratio of 5:1 (Fig. 7a), most of the LZO particles exhibited irregular shapes with sizes of 100–300 nm, but some exhibited a polyhedral or octahedral structure (indicated by the dashed circle in the inset image). On the other hand, in the sample prepared at 1200 °C with the salt/reactant ratio of 3:1, most of the LZO particles exhibited a well-crystallized octahedral structure, with sizes of 300 to 600 nm (Fig. 7b). These results, along with the XRD results (Figs. 3&5), confirmed the high crystallinity of as-prepared LZO particles.

TEM (Fig. 8) further shows that the particle size of LZO was 100–300 nm in the sample prepared at 1100 °C with the salt/reactant ratio of 5:1, whereas that in the sample prepared at 1200 °C with the salt/reactant ratio of 3:1 was 200–500 nm. The SAED patterns along the $[01\bar{1}]$ zone axis (the insets) show clear diffraction spots, indicating the single-crystalline nature of the as-prepared LZO. The two measured angles at about 53.4° (in the inset of Fig. 8a) and 38.1° (in the inset of Fig. 8b) from the Bragg spots agreed well with the expected angles between the (400) and (222) planes and (311) and (222) planes of LZO, further confirming the successful preparation of LZO via the present MSS process.

3.5 Synthesis mechanism of LZO powders

Since the eutectic point of the NaCl–KCl–NaF system is ~548 °C, a molten salt reaction medium would be formed at the test temperatures (900–1200 °C). Thermodynamic calculations indicate that Reaction (1) could occur at as low as room temperature [22, 23]. However, due to the kinetic reason, e.g. low solubilities and slow diffusion of the reactants in the molten salt medium, only a small amount of LZO was formed even at 900 °C (Fig. 3). According to Figs. 3&5, to synthesize phase pure LZO, the temperature had to be increased to 1100–1200 °C.

As shown in Figs. 3&5, intermediate LaOF appeared in the samples after 3 h firing at 900–1100 °C but disappeared at 1200 °C. The reason for this was that LaOF was initially formed from the reaction between fluoride salts and La_2O_3 (reaction (2)) but was further converted later to LZO (reaction (3)).

As reported previously, solubilities of reactants in the molten salt play an important role in MSS [24, 25], depending on which, one of the two important mechanisms, “dissolution and precipitation” and “template-growth”, will function and dominate the MSS process. As a result, product phases with different morphologies can be obtained [26].

To assist revealing the formation mechanism in the present case, ZrO_2 and La_2O_3 raw materials powders were individually heated at 1200 °C for 3 h in NaCl–KCl–NaF. Their morphologies before and after this heat-treatment were examined and compared. As shown in Fig. 9a, the raw ZrO_2 powders consisted of nano-crystalline ZrO_2 smaller than 100 nm, and the raw La_2O_3 powders showed a spongy-like structure with the average size of about 1 μm (Fig. 9b). After firing at 1200 °C in NaCl–KCl–NaF, ZrO_2 retained its original chemical composition (the inset in Fig. 10a) and exhibited a well-crystallized octahedral structure. Also, its particle size increased from about 100 nm to about 5 μm . In the case of La_2O_3 , after heating at 1200 °C in NaCl–KCl–NaF, it was partially converted to LaOF (indicated by the inset EDS in Fig. 10b) with a wide size distribution and a spheroid structure. The remaining La_2O_3 exhibited a platelet-like morphology, with sizes of several microns. Comparing Figs. 9a–b with Figs. 10a–b reveals that the morphologies of starting ZrO_2 and La_2O_3 were quite different from those of ZrO_2 and La_2O_3 heated at 1200 °C in NaCl–KCl–NaF, indicating that ZrO_2 and La_2O_3 had at least some solubility in the molten NaCl–KCl–NaF. This, along with the fact that as-synthesized LZO had different shapes and sizes (Fig. 7) from those of the as-received ZrO_2 and La_2O_3 (Fig. 9), suggested that the “dissolution-precipitation” mechanism had played a dominant role in the MSS of LZO.

Based on the relevant formation mechanisms proposed previously [24, 25] and the results presented and discussed above, a plausible mechanism for the whole MSS process can be illustrated schematically in Fig. 11 and described as follows: ZrO_2 and La_2O_3 partially dissolved and were then mixed homogeneously in the molten salt at the atomic level (Fig. 11a). Consequently, they would rapidly react with each other to form LZO in the molten salt according to reaction (1) or (3) (Fig. 11b). Once the molten salt had been oversaturated with LZO, LZO crystals would start to precipitate from the salt. The precipitation of LZO from the oversaturated salt would lead to further dissolution and reaction of ZrO_2 and La_2O_3 (or LaOF), which would accordingly lead to the formation of more LZO (Fig. 11b). These processes would be repeated again and again until all of the ZrO_2 and La_2O_3 reactants had been completely consumed and phase pure LZO obtained (Fig. 11c).

4 Conclusion

$\text{La}_2\text{Zr}_2\text{O}_7$ ultrafine powders were successfully synthesized via a simple molten salt process using zirconium oxide and lanthanum oxide as raw materials, and sodium chloride, potassium chloride and sodium fluoride to form a reaction medium. The lowest synthesis temperature (1100 °C) was much lower than required by the conventional solid-state mixing method and most of the wet-chemical techniques. The NaCl-KCl-NaF ternary salt effectively accelerated the synthesis of LZO and use of appropriately higher amount of molten salt was more beneficial for the LZO formation. Phase pure LZO ultrafine powders with crystalline size of 100–300 nm were synthesized at 1100 °C. The “dissolution-precipitation” mechanism had played an important role in the synthesis.

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Table and Figure Captions

Table 1 Batch compositions of samples and their firing conditions.

Figure 1 XRD patterns of samples resultant from 3 h firing at 1100 °C with various types of salts.

Figure 2 Relative contents of crystalline phases calculated from XRD patterns shown in Fig. 1.

Figure 3 XRD patterns of samples resultant from 3 h firing at various temperatures in NaCl–KCl–NaF.

Figure 4 Relative contents of crystalline phases calculated from XRD patterns shown in Fig. 3.

Figure 5 XRD patterns of samples resultant from 3 h firing at 1100 °C with various salt/reactant weight ratios in NaCl–KCl–NaF.

Figure 6 Relative contents of crystalline phases calculated from XRD patterns shown in Fig. 5.

Figure 7 FE–SEM images of the samples resultant from 3h firing (a) at 1100°C with the salt/reactant ratio of 5:1, and (b) at 1200 °C with the salt/reactant ratio of 3:1.

Figure 8 TEM images of LZO powders prepared at (a) 1100 °C with the salt/reactant weight ratio of 5:1, and (b) 1200 °C with the salt/reactant weight ratio of 3:1. (The insets show the SAED patterns from $[01\bar{1}]$ zone axis.)

Figure 9 FE–SEM images of raw materials (a) ZrO_2 and (b) La_2O_3 .

Figure 10 FE–SEM images of (a) ZrO_2 and (b) La_2O_3 individually heated at 1200 °C in NaCl–KCl–NaF.

Figure 11 A schematic of the MSS process of LZO ultrafine powders.

Table 1

Codes	Firing conditions	Salt assembly	Ratio of salt to
		(weight ratio)	reactant (Wt. %)
S1	1100 °C/3 h	KCl–LiCl (0.55:0.45)	5:1
S2	1100 °C/3 h	Na ₂ CO ₃ –K ₂ CO ₃ (0.49:0.51)	5:1
S3	1100 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	5:1
T1	900 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	3:1
T2	1000 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	3:1
T3	1100 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	3:1
T4	1200 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	3:1
RS0	1100 °C/3 h	No Salt	—
RS1	1100 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	1:1
RS3	1100 °C/3 h	NaCl–KCl–NaF (0.10:0.58:0.32)	5:1

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11