Physicochemical Properties of Single Phase $\text{La}_2\text{Zr}_2\text{O}_7$ Powder^{*1}

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Powders of La_2O_3 and ZrO_2 in ethanol based suspension were planetary ball milled at 200 rpm for 12 hours, dried and then heat treated at 1500°C for one hour to synthesize single phase of $\text{La}_2\text{Zr}_2\text{O}_7$ which is a very promising thermal barrier coating material. Planetary milling results to particle diminution together with an increase in surface area with increasing milling time as investigated by FE-SEM, particle size analyses and BET method. The formation of single phase $\text{La}_2\text{Zr}_2\text{O}_7$ with pyrochlore structure was confirmed by X-ray diffraction and TEM analyses. DSC investigation on the milled powders revealed the dehydroxylation reaction at around 320°C and complete disintegration of ethanol including decarboxylation at around 500°C . The absence of these peaks in the thermal plot for the single phase material confirms its thermal stability at 1500°C sintering temperature.

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1. Introduction

Lanthanum zirconate, $\text{La}_2\text{Zr}_2\text{O}_7$ having a cubic pyrochlore structure has recently found many interesting industrial applications including thermal barrier coating (TBC)¹⁻³ and nuclear waste encapsulation.⁴⁻⁶ It has gained widespread research attention due to its remarkable properties like very high thermal stability, low sintering, low thermal conductivity, no permeability of oxygen and excellent stability.⁶⁻⁸

Preparation of this material has been done through solid-state reaction⁹⁻¹² and other wet-chemistry-based routes, which include co-precipitation,^{12,13} sol-gel process,^{12,14,15} hydrazine¹⁶ and citrate methods.¹³ Each of these preparation techniques has its own advantages and disadvantages like the high temperature treatment for usual direct solid state reaction leads to particle agglomeration, whereas wet-chemistry-based routes usually use expensive and environment-sensitive chemicals.¹⁷ Lately, mechanochemical (MC) synthesis of $\text{La}_2\text{Zr}_2\text{O}_7$ by dry method had been attempted to avoid these disadvantages, however failed to produce single phase powder.¹⁸ Another method of preparation was able to produce single phase material by combination of mechanical activation of the starting powders in wet state followed by drying and solid-state sintering.¹¹ The time requirements however for mechanochemical activation and subsequent sintering reactions are very long.

Recently, a wet mechanochemical route has been optimized to determine as much as possible the least reaction time and energy to synthesize single phase of lanthanum zirconate.¹⁹ Several milling conditions including ball to powder ratio, milling speed, milling time and size of grinding media were varied to produce a well homogenized product. This paper will report on the evolution of single phase $\text{La}_2\text{Zr}_2\text{O}_7$ powder prepared using the optimized wet MC process, particularly on the physicochemical properties of the synthesized material as a function of milling time at 200 rpm.

2. Experimental Procedure

An ethanol based suspension of La_2O_3 (High Purity Chemicals) and ZrO_2 (Tosoh) powders was prepared prior to wet MC treatment in a planetary ball mill (Fritsch Pulverisette) at 200 rpm up to 12 hours using zirconia pot (250 mL) and balls (5 mm). Both powders were preheated at 1100°C for one hour to remove the hydroxide components for stoichiometric weighing. The ball to powder ratio is equal to 10:1 while the mill charge is about 60% of the total volume of the zirconia pot. These are the specifications of the wet MC method which have been determined through an optimization process to produce single phase of lanthanum zirconate.¹⁹ The cumulative particle size distributions of the powders in the milled slurries were determined using a laser particle size analyzer (Helos system). The slurries were then dried at 110°C for 24 hours in an oven then heat treated at 1500°C for one hour. Structural analysis was performed using XRD (Rigaku) and TEM (Jeol), while the morphological transformation was investigated using FE-SEM (Jeol) and surface area by BET method (Shimadzu chromatograph). The thermal behavior of the milled powders was investigated by a differential scanning calorimeter (Seiko, DSC6300) using platinum crucibles at a heating rate of $10^\circ\text{C min}^{-1}$.

3. Results and Discussion

The effect of planetary milling on the particle morphology is manifested by the particle diminution as shown in the FE-SEM micrographs in Fig. 1. Considerable damage on La_2O_3 can be observed at increasing milling time, while the ZrO_2 particles become undistinguishable as products of mechanical activation in the form of white spherical powders are increased.

Figure 2 shows the very narrow cumulative particle size distribution of the milled powders. It can be observed that with milling time longer than one hour, the particle size distribution becomes narrower which implies that the powders in the milled slurries are homogeneously distributed. An inset graph shows that the average particle size initially decreases then slightly increases with further milling

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Fig. 1 FE-SEM micrographs of (a) the raw mixture and (b)–(f) powders after planetary milling for 1, 3, 6, 9 and 12 hours.

Fig. 2 Cumulative curves of the particle size distribution after different milling times.

Fig. 3 Specific surface area of the powders after different milling times.

longer than six hours. The BET specific surface area (Fig. 3), however, increased with increasing milling time, which indicates that intra-particle porosity also increased.²⁰⁾

The X-ray diffraction profiles after increasing milling time (Fig. 4) show an important decrease of the peak intensities

relative to the raw mixture, indicating loss of crystallinity. $\text{La}(\text{OH})_3$ phase also evolved after wet MC treatment. A few peaks of La_2O_3 are still detected after one hour but disappeared on further milling. On the other hand, the presence of relatively lower intensity ZrO_2 peaks after

Fig. 4 X-ray diffraction profiles of planetary milled powders with increasing milling time.

Fig. 5 X-ray diffraction profiles of powders sintered at 1500°C with increasing milling time.

milling indicates lack of efficiency of the grinding process; this being attributed to the intrinsic structure and hardness of the starting powder. Figure 4 confirms the observation in Fig. 1 that La_2O_3 underwent greater structural damage than ZrO_2 as manifested by the disappearance of the La_2O_3 XRD peaks.

Sintering the raw mixture at 1500°C for one hour produced small peaks of $\text{La}_2\text{Zr}_2\text{O}_7$ as shown in Fig. 5. However, with prior MC treatment even at a minimum time of one hour, very crystalline $\text{La}_2\text{Zr}_2\text{O}_7$ were produced together with small

Fig. 6 Electron diffraction pattern of the synthesized single phase $\text{La}_2\text{Zr}_2\text{O}_7$ powders which underwent (a) 9 hrs and (b) 12 hours milling, typical for pyrochlore structure.

Fig. 7 DSC curves of the planetary milled powders with increasing milling time.

traces of free La_2O_3 and ZrO_2 . Single phase $\text{La}_2\text{Zr}_2\text{O}_7$ was formed upon heat treatment of the powder milled after nine hours which is even shorter than the previously reported results of the optimized wet MC process.¹⁹⁾ X-ray diffraction analysis on this material reveals that all its peaks match with the entry in the JCPDS card number 73-2363 indicating that the synthesized material is single phase $\text{La}_2\text{Zr}_2\text{O}_7$ with cubic pyrochlore structure.²¹⁾ This result is further confirmed by its electron diffraction pattern in Fig. 6; typical for pyrochlore structure. The same XRD and TEM findings were obtained for the powder milled after 12 hours.

The DSC curves of the milled powders as a function of milling time (Fig. 7) show two endothermic peaks. The first is at around 320°C corresponding to dehydroxylation of $\text{La}(\text{OH})_3$.¹⁶⁾ The second one is at around 500°C corresponding to decarboxylation and complete disintegration of ethanol. The DSC curve for zero milling time was taken using the unpreheated powder precursors to determine the initial reactions of the powder on heating. The thermal peaks reveal similar initial reactions as with the milled powders due to the presence of initial small amounts of $\text{La}(\text{OH})_3$ in La_2O_3 ; owing to its high reactivity with moisture in air. The second peak was due to decarboxylation from reaction with carbon in air. These endothermic peaks upon milling are of higher reaction temperatures due to interaction with ethanol, but shift to lower temperatures with the increase of milling time. For the DSC plot of the single phase powder, these peaks are

not detected confirming its thermal stability at 1500°C.

Mechanochemical activation of the starting powders enhances reactivity, which is evident in the XRD profiles and the DSC thermal plots. This is due to the reduction of the energy necessary to destroy the crystalline structure of the materials²⁰⁾ through planetary milling, making it easier for the subsequent solid-state reaction to proceed during heat treatment.

Thus, it is very ideal to produce a well homogenized powder mixture preferably with very narrow particle size distribution and very large specific surface area through an initial wet mechanochemical activation in a planetary ball mill to easily obtain the single phase $\text{La}_2\text{Zr}_2\text{O}_7$ powder on sintering.

4. Conclusion

La_2O_3 and ZrO_2 powders in ethanol-based suspension were easily activated by the wet MC method using a planetary ball mill. During milling the starting powders decreased in particle size and increased in surface area with corresponding loss of their crystallinity. On subsequent heat treatment at 1500°C for one hour, single phase $\text{La}_2\text{Zr}_2\text{O}_7$ with pyrochlore structure was formed. The single phase powder is thermally stable at this temperature.

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