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Effect of the formation parameters on the thermal properties of $\text{La}_2\text{Zr}_2\text{O}_7$

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Abstract Lanthanum zirconates has been suggested as a thermal barrier coating for many high temperature applications. This study is focusing on the effect of different preparation parameters on the thermal conductivity of $\text{La}_2\text{Zr}_2\text{O}_7$. We have used solid state reaction to form the zirconates powder was very good homogeneity. We have studied the effect of the intimal $\text{ZrO}_2/\text{La}_2\text{O}_3$ ratio, and found the 50% to be the optimum. The effect of the sintering temperature has also been studied and 1100°C was chosen as the optimum sintering temperature. The sintering time was also studied, where 3 hours was proved to be enough to obtain a homogeneous single phase compound with affordable method.

Keywords: Ceramic composites, Sintering, Thermal properties, Thermodynamics and kinetics of processes in materials

1. Introduction

Rare earth zirconates have received considerable attention due to its wide industrial applications such as solid oxide fuel cell electrode materials, fluorescence screens, thermal – barrier coatings, high temperature heating elements, and oxidation catalysts.[1-3] Of particular interest, lanthanum zirconate, $\text{La}_2\text{Zr}_2\text{O}_7$, LZ has been suggested as an alternative to the traditional NiCoCrAlY coating on super alloys as a thermal barrier in modern gas-turbine engines.[2, 4] LZ exhibits high thermal stability nearly up to its melting point at 2300°C . The thermal conductivity of LZ is as low as $1.56 \text{ W m}^{-1} \text{ K}^{-1}$ that is much lower than that of yettria stabilised zirconia ($2.12 \text{ W m}^{-1} \text{ K}^{-1}$).[5-7] LZ has low sintering rate, which helps on the formation of films without damaging the substrate. However, LZ suffers from low thermal expansion coefficient ($9 \times 10^{-6} \text{ K}^{-1}$), which makes the coating more susceptible to thermal stress due to the large thermal expansion mismatch with the metallic substrates.[6, 8, 9]

There have been several attempts to minimise the effect of the thermal expansion mismatch between the ceramics and the substrate. Using nano particles to form a more robust structures of the coating has shown great success.[10] Doping the LZ with other rare earth elements also proven to be successful strategy to increase the thermal expansion coefficient and subsequently improve the coating stability.[11, 12] Other techniques such as graded coatings and double-ceramic-layer coatings in which LZ is coated on YSZ inner layer, has also been used industrially.[13-16] Amongst the other thermal properties modifiers, doping with other rare earth is gaining more attention since it usually associated with less problem during the fabrication.

The present paper has a more economic strategy of using the other rare earth oxides exists in the natural mineral to increase the thermal expansion coefficient. The paper also is investigating different parameters that might affect the thermal conductivity of the LZ. The present work adopted simple solid-state reaction process to prepare the RE-doped LZ.



2. Experimental work

2.1. Preformation calculations

Before proceeding to the formation of the LZ from natural ore, a comprehensive array of calculation was carried out in order to have a pre-estimation of the materials preparation conditions HSC chemistry-5 was used to calculate the thermodynamic parameters at different reaction temperatures. The calculations showed that it is possible to form the single phase compound even at room temperature. Although increasing the sintering temperature seems to have a small effect on the delta G (which reflect the spontaneity of the reaction), the reaction kinetic seems to increase significantly with the temperature. From the resulted change in enthalpy values we deduce that the reaction is exothermic, the entropy values behaved as positive values at temperature range from zero to 1100 °C, and started to be negative at 1200 °C ,which means that the system is not controllable at temperature more than 1200 °C, so it is recommended to apply the sintering of the reactants at temperature less than 1200 °C

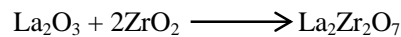


Table 1: Showing the values of free energy, enthalpy, entropy and equilibrium constant for the lanthanum zirconate at different temperatures

T, °C	ΔH, kJ	ΔS, J/K	ΔG, kJ	K	Log(K)
0	-86.800	9.960	-89.521	1.320 E+17	17.121
100	-86.800	9.960	-90.517	4.697 E+12	12.672
200	-86.800	9.960	-91.513	1.270 E+10	10.104
300	-86.800	9.960	-92.509	2.701 E+8	8.432
400	-86.801	9.959	-93.505	1.804 E+7	7.256
500	-86.801	9.959	-94.501	2.427 E+6	6.385
600	-86.801	9.959	-95.497	5.169 E+5	5.713
700	-86.801	9.959	-96.492	1.513 E+5	5.180
800	-86.801	9.959	-97.488	5.566 E+4	4.746
900	-86.801	9.958	-98.484	2.429 E+4	4.385
1000	-86.802	9.958	-99.480	1.207 E+4	4.082
1100	-86.802	9.958	-100.476	6.644 E+3	3.822
1200	-103.442	-1.558	-101.146	3.861 E+3	3.587
1300	-102.746	-1.102	-101.012	2.261 E+3	3.354
1400	-101.855	-0.553	-100.929	1.416 E+3	3.151
1500	-100.770	0.076	-100.904	9.392 E+2	2.973

2.2. Experimental and methodology procedure

The experimental work and methodology reprints on the materials processing, dehydration, hydropressing, sintering and instrumental investigation by XRD, SEM and thermal conductivity measurement device. The starting materials to be processed; are lanthanum oxide and zirconium oxide with a commercial grade brand name ALDRICH™ with a purity 99% with using screen analysis for controlling mesh size up to -63 micron, both two materials were mixed and grinded inside discmill for two hours in dry atmosphere, after finishing mixing by mechanical grinding the loosed sample was released off and weighed to be 10 grams, then the sample was dried inside oven to a temperature up to 100 °C, the dried sample was mixed with bindery materials paraffin wax with a weight percentage up to 1.5%; estimated as function of the total weight of the sample, then the sample was mounted inside a die with a dimension 23mm diameter and 12 mm height, the pressing applied load estimated to be 15 ton, this procedure was repeated with different materials balance, where we used lanthanum different weighing percentages, where the mixing process used 20%,

30%,40%,50%, and 60% lanathanum oxide and the balance was zirconium oxide, ie the mixinxg process was repeated five tiems with different starting materials weight balance.eache weight of mixed materaisl was repeated also five times to prduce five samples with the same materials balance to study subsequently the effect of sintering temperature.the pressed samples was sintered at different temperatures to test the effect of sintering temperatures ,the sintering was done at muffle furnace at temperature 900°C,950 °C,1000 °C,1050 °C, and 1100 °C, eventually each five samples was sintered at these five sintering temperature. The sequence of the process is illustaring in flowsheet at figure (1).

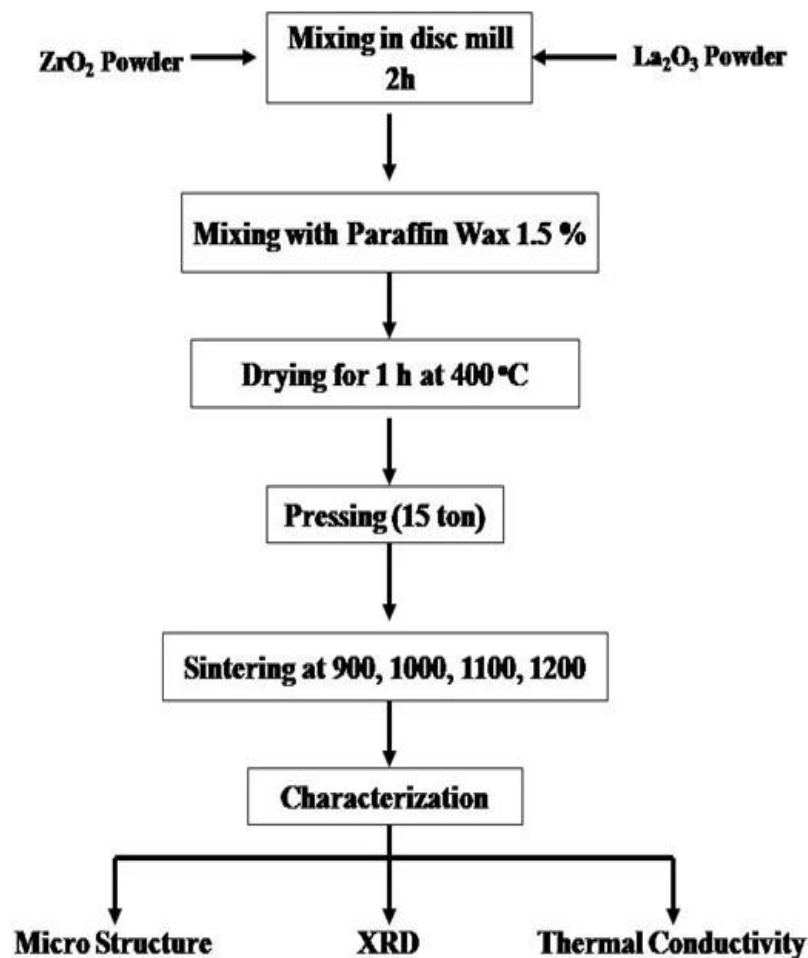


Figure1. Simple flow sheet for pressing and sintering process

Each produced sample was investigated by X-ray powder diffraction (XRD) measurements were carried out with a Philips x-ray generator model PW 3710=31 a diffractometer with automatic sample changer model PW1775 (scintillation counter, Cu-target tube and Ni-filter at 40KV and 30 mA). Energy dispersive x-ray measurements were measured using environmental scanning electron microscope (ESEM) EXL 130 and attached by energy dispersive spectrometry (EDX) unit system.

Thermal conductivity of each test sample was measure and detected by diffuse meter measure flash used to measure the heat transferred through the sample thickness for this purpose the apparatus theheat flux diffusion froDXF 200 employs a High Speed Xenon-pulse Delivery source (HSXD) each

sample was mounted and measure the heat flux diffusion and the calculation of heat diffusion showed the that the thermal conductivity varied from sample to another.

3. Ruselts and Discution

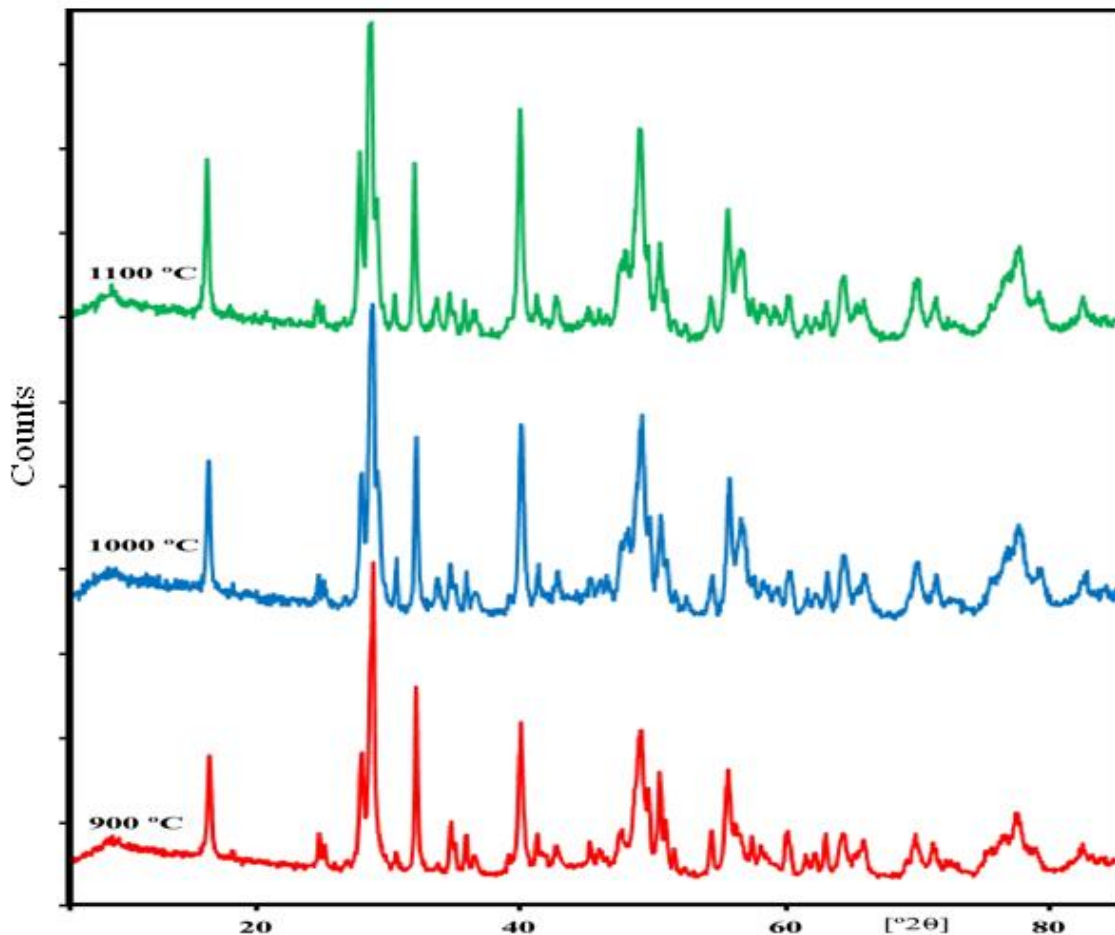


Figure 2. XRD patterns of $\text{La}_2\text{Zr}_2\text{O}_7$ at diffeent sintiring temperature

The XRD patterns of $\text{La}_2\text{Zr}_2\text{O}_7$ ceramics under deffernt sintring conditions are shown in figure 2. All the defraction peaks can be fitted with the typical pyrochlor LZ pattern (JCPDS 73 -0444), [17, 18] sugesting succesful formation of the single phase oxide. The intensity of the peaks and the width at half length decreased with increasing the sintiring temprture, which is a sign of increasing the crystallinity. The lattice parameter evaluated from the X ray deffraction pattern are $a = 1.0823 \text{ nm}$, $b = 1.0823 \text{ nm}$, $c = 1.0823 \text{ nm}$, which is very close to the reported values of the LZ lattace. [17] This bascially means that the presence of impurties did not change the cyrstal structure or reduced the ordering of the atoms. We can then conclude that the other RE impurties are occupying the La^{+3} ions posation, i.e. they are packed in the vacancy of the octahedron constituted by 6ZrO_6 in the pyrochlor crystal structure. Indeed this substitution of the La^{+3} ions with lower valence ions creates oxygen vecancies, which is curcial for controlling the conductivity proprties and the thermal expansion coffecient. [19]

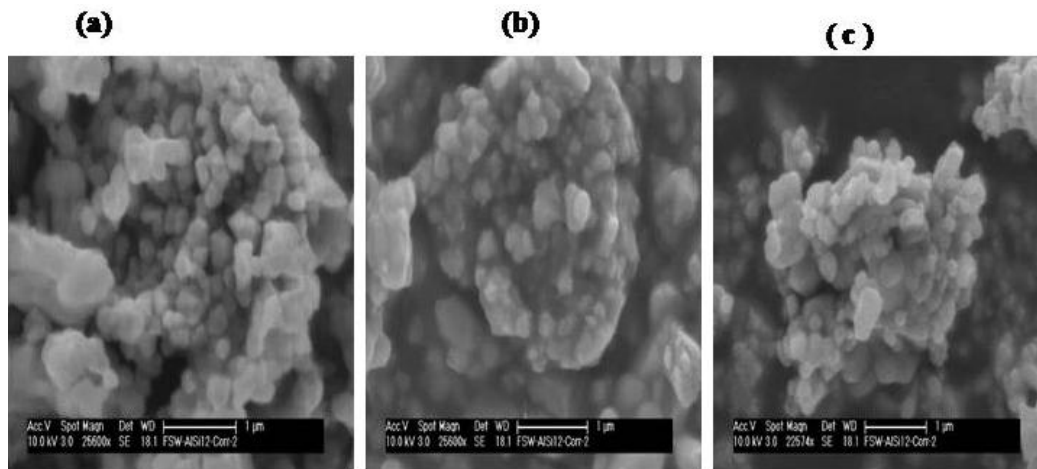


Figure 3: Shows microstructures using SEM of $\text{La}_2\text{Zr}_2\text{O}_7$ ceramics at content of La_2O_3 50% in matrix under different sintering conditions : a)- at 900 °C, b)- at 1000 °C and c)- at 1100 °C all for 3 h

The changes in the microstructure of lanthanum zirconate with the sintering temperatures are evaluated using scanning electron microscope. Figure (3) shows that the particles size are growing with increasing the sintering temperature. For the low temperature sintering, the grain boundary is very clear, indicating very low sinterability of the powder. Increasing the sintering temperature leads to aggregation of the particles into bigger clusters. The grain boundary almost vanished for the sample heated at 1200 indicating the small particles are in growing state to a larger particle. The bulk density of the particles also increased with increasing the temperature, which probably due to the compacting of the particles and the reduction of the between – the-particles porous. [20]

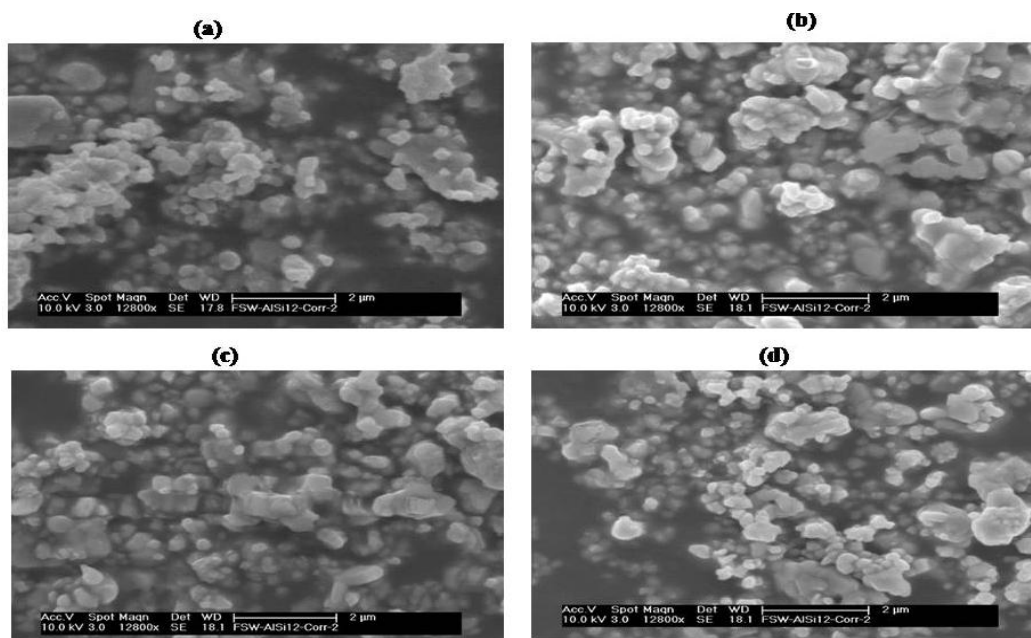


Figure 4: Shows the microstructure using SEM of $\text{La}_2\text{Zr}_2\text{O}_7$ at sintering temperature 1100 °C at 3h and different content of La_2O_3 in matrix: a)- at 30% , b)- at 40% , c) – at 50% and d)- at 60%.

Figure 4 shows the SEM images of the LZ powder with various La_2O_3 content all sintered at 1100 °C. It seems like the percentage of the La_2O_3 is less pronounced than the sintering temperature on the microstructure of the prepared LZ powder. This is mainly because both components of the single

oxides phase have very similar melting point and particle size. There are slightly tendency to form bigger aggregation with increasing the rare earth content. La_2O_3 may disproportionate to LaO_2 and LaO , which may accelarte the reaction with the zirconium oxide to form non-stoichiometric oxide phase, which usually have lower melting point than the more ordered oxide phase ($\text{La}_2\text{Zr}_2\text{O}_7$).

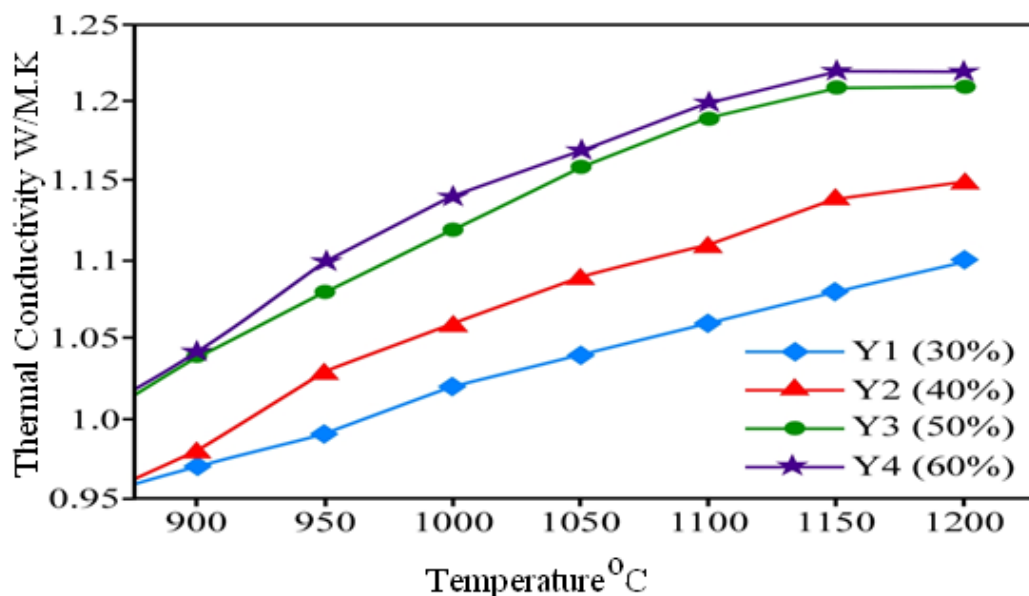


Figure 5. Thermal conductivity at various sintering temperature and different of La_2O_3 content

The thermal conductivity of the sample with various La_2O_3 content sintered at different temperature are illustrated in figure 5. The thermal conductivity measurements were conducted using the diffuse-meter technique. Clearly the thermal conductivity increased with increasing the temperature due to the decrease of the boundary effect with the growth of the particles size. The conductivity increased also with increasing the La_2O_3 content. By almost of 30 % at any temperature, we believe that the increase of the thermal conductivity is related to introducing lattice defects, including oxygen vacancies, which can changes the energy state of the binary oxide. Interestingly the thermal conductivity value measured in the current work is much higher than that reported in the literature.[21] We believe the enhanced thermal conductivity is due to the increase of the oxygen vacancies and other disorders in the LZ lattice with increasing the doping by the other RE oxides.[22]

4. Conclusion

We have successfully produced pure phase of $\text{La}_2\text{Zr}_2\text{O}_7$ using facial and simple solid stat reaction. The results of the current work showed that the most homogeneous phase can be produced by mixing the stoichiometric amount of the La_2O_3 and ZrO_2 . The morphology of the particles was found to be dependent on the sintering temperature, with tendency of the particles to form large clusters and grow in size. Interestingly, we found that the impurities associated with La_2O_3 have a significant role on increasing the density of the oxygen vacancies and other defects in the $\text{La}_2\text{Zr}_2\text{O}_7$ cubic lttice. The slightly lactice dystortion has a significant role on increasing thermal conductivity to reach a maximum value of 1.22 W/m.k.

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