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Characterization and densification of lanthana–zirconia powders prepared by high temperature hydrolysis

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Zirconia–lanthana powders containing 4.5, 7, 10, 15 and 20 mol% La_2O_3 were prepared by hydrolysis. The hydrolysis process was carried out in a laboratory stainless steel autoclave for their equivalent hydroxides for 2 h at 200° C. The powders were investigated using X-ray diffraction, infrared spectrometry, and transmission electron microscopy techniques. No other phases except the cubic phase zirconia of fluorite-type structure were detected. The prepared materials were examined for their thermal stability and phase constitution, by X-ray and infrared analyses, on heating up to 1400° C. The cubic phase zirconia remains stable up to 1000° C at which it starts to decompose yielding monoclinic zirconia and lanthanum zirconate. At 1200° C, the cubic phase nearly disappears in the sample containing 4.5 mol% La_2O_3. Increasing La_2O_3 content up to 20 mol% retards its destabilization, reduces the yielded monoclinic phase, and in the same time increases the formed lanthanum zirconate phase. At 1500° C only monoclinic ZrO_2 and $La_2Zr_2O_7$ are present. The $La_2Zr_2O_7$/monoclinic ZrO_2 ratio increases with increasing La_2O_3 content. Pressed specimens of the prepared materials were fired for 2 h at 800 to 1400° C. The sintering activity of the prepared powders resulted in a 92% theoretical density body for the 4.5 mol% ZrO_2 material. The densification properties in relation to changes in the phase constitution are discussed.

1. Introduction

Few materials show as much potential for advanced high temperature applications as zirconia-based ceramics. The high melting point and chemical inertness of the stabilized cubic fluorite structure zirconia are the basis for its extensive use as a refractory material. The fundamental concept in zirconia ceramics is to alloy pure zirconia with enough of another oxide to fully or partially stabilize the high temperature polymorph of zirconia to lower temperature. A large amount of research have been made on the stabilization of zirconia by oxides such as calcia, magnesia, yttria, and rare earth oxides [1–4].

The system ZrO_2–La_2O_3 has been studied by several investigators. Trombe and Foëx [5] found that the cubic fluorite solid solutions exist between 10 and 35 mol% after melting and between 25 and 40 mol% at 2000° C. Brown and Duwez [6] found that a minimum of 30 mol% lanthana is required to form the cubic solution at 980° C. Roth [7] has shown that instead of the fluorite solid solutions, solutions based on the compound $La_2Zr_2O_7$ which has the cubic pyrochlore structure form in this system. The work of Perez and co-workers [8–10] has verified the existence of this compound. They found that the cubic fluorite structure is stable only above 1800° C and extends from 6 to 16 mol% La_2O_3 near the liquidus temperature. Strickler and Carlson [11] detected only pyrochlore structures in samples containing between 6 and 24 mol% La_2O_3 fired at 1800 to 2000° C. In another phase study of this system [12, 13], the fluorite type solid solutions have been observed at about 14 mol% La_2O_3. Rouanet [14] placed the eutectic point at 1850° C with 5 mol% La_2O_3 and found the fluorite phase to be stable from 4 to 8 mol% and 2 to 18 mol% La_2O_3 at 2000 and 2200° C, respectively.

The inconsistancies in the results within the ZrO_2–La_2O_3 system necessitates further investigation. Furthermore, the unique refractory properties of the cubic ZrO_2 solid solutions decrease by increasing the amount of added La_2O_3. The recent ceramic technology stresses on manufacturing of highly refractive ceramic materials at moderate temperatures and with suitable microstructural properties. The employment of the ultrafine and homogeneous powders prepared by the so-called wet chemical methods proved to be efficient to satify this demand. Many wet chemical procedures [15–17] have been considered for the preparation of fine powders of stabilized zirconias. These methods have also proved to be successful in decreasing the amount of oxides needed to stabilize zirconia. However, the precipitates prepared by such methods require a subsequent calcination step to obtain the corresponding oxides. This step may lead to the formation of undesirable hard agglomerates before processing. Recently, a method of preparation of yttira stabilized zirconia was developed [18] in which the hydroxides of the precursors were hydrolysed by autoclaving under suitable pressure. This method avoids the undesirable calcination step. Fully stabilized

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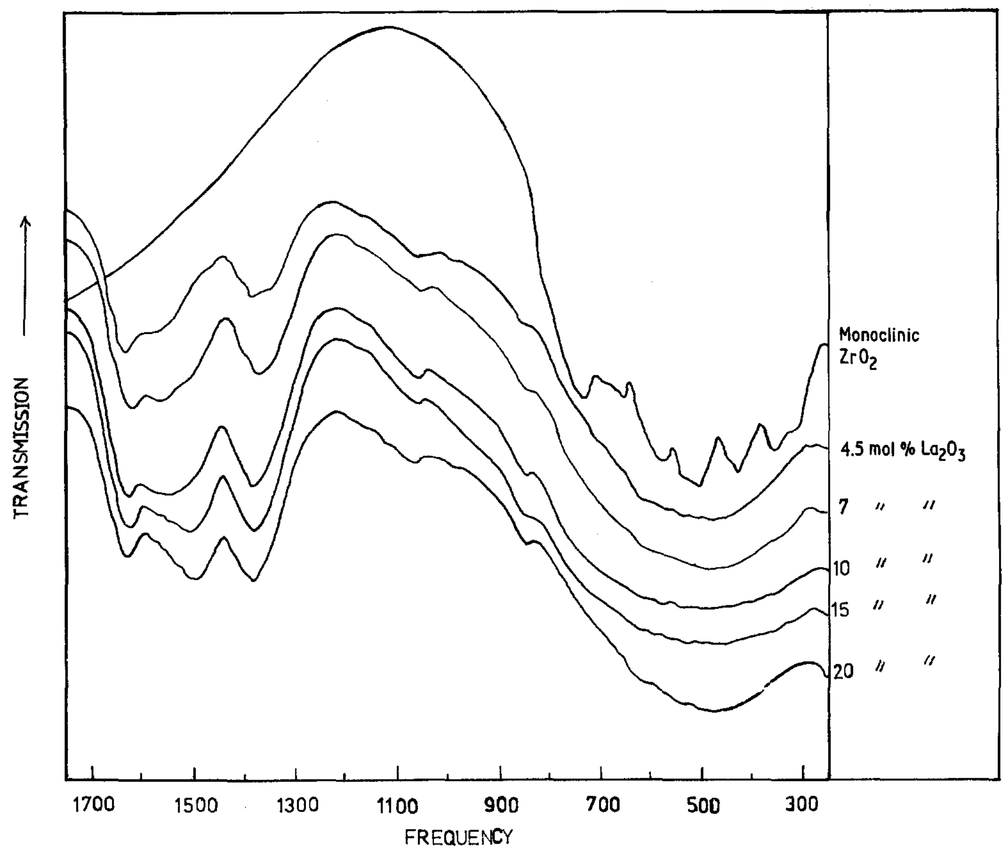

Figure 1 Powder diffraction transmission spectra of as-prepared powders.

fine zirconia powder containing only 4 mol % Y_2O_3 was prepared by this method [19].

In the present work, ultrafine zirconia–lanthana solid solution powders have been prepared by autoclaving their equivalent hydroxides at 200° C for 2 h. The obtained powders were characterized, examined for their thermal stability and used to form dense ceramic bodies. The sinterability and densification properties of the fired ceramic bodies were studied.

2. Experimental details

Five zirconia–lanthana mixtures were prepared with lanthana concentrations of 4.5, 7, 10, 15 and 20 mol % of the mixtures. A laboratory stainless steel autoclave (50 cm^3) and an electrically heated oven were used for the hydrolysis reaction. Standard preparations were performed as follows:

1. Solutions of analytically pure* zirconium oxychloride and lanthanum trichloride were separately prepared and then mixed at the required ratios. Concentrated NH_4OH solution was added dropwise to the well stirred mixture until the pH value reached 10.
2. Excess ammonia was added to ensure complete precipitation of both zirconium and lanthanum ions and the conditions were kept ammoniacal to the end of the reaction to avoid any back dissolution of the La^{3+} ions in the acidic medium [20, 21]. The batch concentration was kept at 12.5% during all the preparations and no certain gas atmosphere was used.
3. The white precipitate formed was then transferred with its mother liquor to the autoclave and the temperature was raised stepwise up to 200° C and the hydrolysis was carried out for 2 h at this temperature.
4. The resulting snow-white well-settled precipitate, in all cases, was filtered from its clear supernatant liquid. It was laundered several times with distilled water until a negative reaction for chloride ions was obtained in the filtrate, and then dried at 120° C for 24 h. No traces of La^{3+} ions were detected in the supernatant liquids throughout all the preparations.

Portions of the prepared dried powders were calcined in air using an electrically heated muffle furnace at temperatures between 300 and 1200° C, for 1 h at each temperature, for the subsequent investigations.

The powders were analysed for their structure using a D500 Siemens X-ray diffractometer (Cu$K\alpha$ radiation and a nickel filter). Infrared (IR) spectra were obtained with a Beckman IR 4250 absorption spectrophotometer. In-line transmission was measured on thin sections (1.00 mm thick) using glass standard. Powder absorption spectra were taken using KBr pellets.

Particle size and shape were studied by an E 10 Zeiss electron transmission microscope. A sample portion of each powder was dispersed in ethyl alcohol using an ultrasonic path for 15 min. Ethyl alcohol produced a better spread of particles on the grid than water or acetone [16].

Cold pressing was carried out uniaxially in a steel dye and a hydraulic press under a pressure of 5000 psi. Pellets of 10 mm diameter and 1.5 mm thickness were fabricated. Sintering was carried out in air at temperatures varying from 800 to 1400° C with 2 h soaking. Bulk densities were measured by the mercury immersion method.

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*More than 99.89% pure according to the supplier (BDH chemicals, Poole, England).

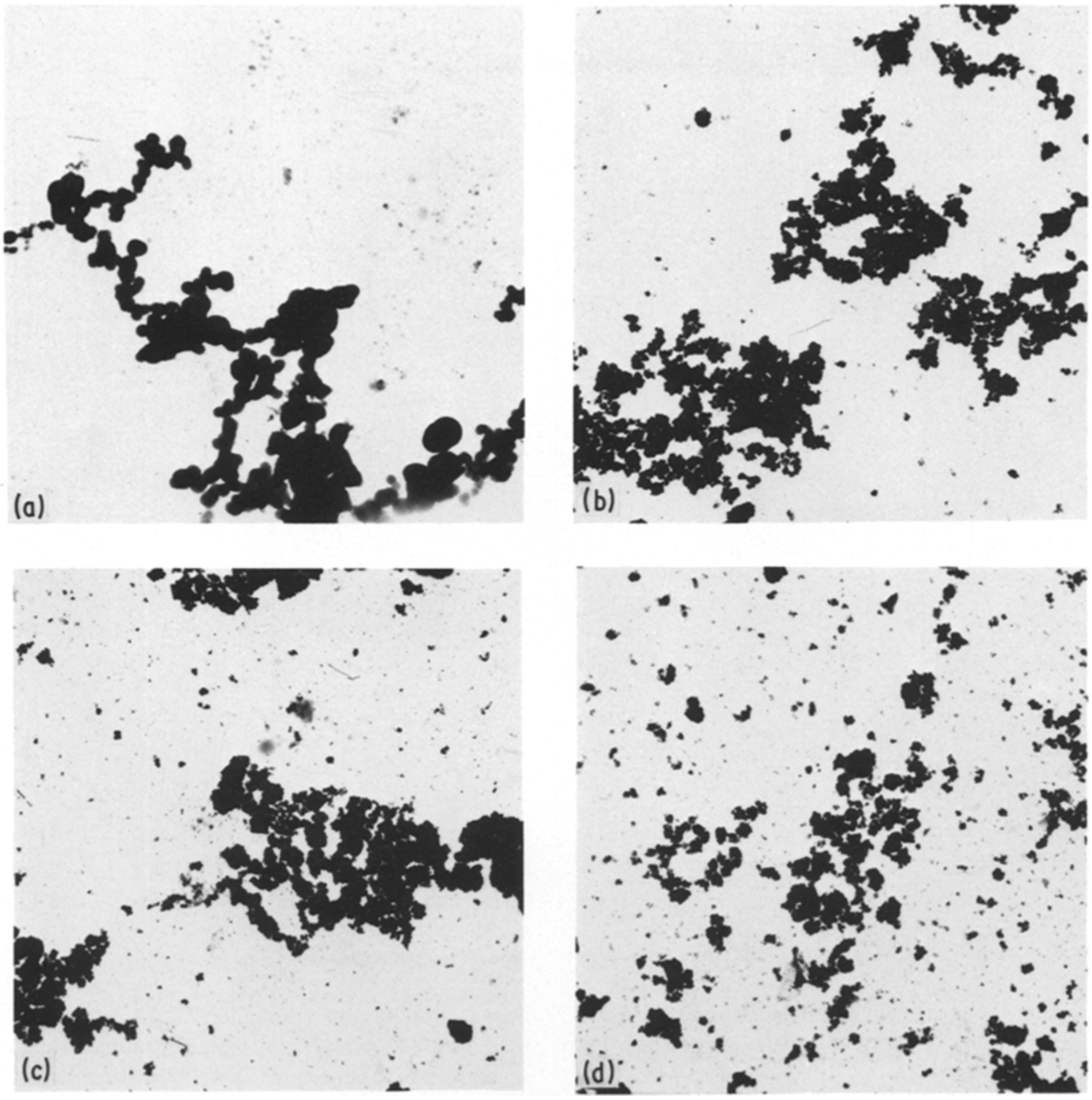

Figure 2 Electron micrographs (× 10.000) of as-prepared powders containing; (a) 4.5 mol %, (b) 10 mol %, (c) 15 mol % and (d) 20 mol % La_2O_3.

3. Results and discussion

3.1. Characterization of the prepared powders

The X-ray diffraction analysis showed that the as-prepared powders are amorphous to X-ray. The IR absorption spectra of the powders are shown in Fig. 1. A monoclinic ZrO_2 spectrum is shown for comparison. Nearly identical spectra are obtained for the five investigated powders. The presence of the broad absorption band at ~600 to 400 cm^{-1}, together with its weak shoulder near 620 cm^{-1}, indicates that full stabilization of the cubic ZrO_2 phase has been achieved [22]. The band at 1630 cm^{-1} is attributed to the adsorbed moisture during the grinding of the samples for IR measurements [23]. The bands around 1520 and 1380 cm^{-1} together with the weaker ones at 1620 and 840 cm^{-1} are attributed to the surface carbonates originated from the adsorption of atmospheric CO_2 [22, 23]. The similarity in the spectra of the prepared materials indicates that the increase in La_2O_3 content from 4.5 to 20 mol % is not accompanied by any observed effect upon the crystal structure of the formed ZrO_2 solid solution phase.

The particles of the prepared powders were studied by the transmission electron microscopy (TEM) at various magnifications and for various fields [24]. Figs 2a to d show electron micrographs of the as-prepared powders. All the powders exhibit particles in the submicron range. The increase in La_2O_3 content is accompanied by a decrease in the particle's agglomeration and size. A sharp decrease in the average of particle size from about 130 to 140 nm for the 4.5 mol % La_2O_3 containing powder to about 60 to 70 nm for the powder containing 7 mol % La_2O_3. The rate of decrease is slowed down for higher La_2O_3 contents so that the average size for 10 mol % La_2O_3 ranges between 60 and 50 nm. The sizes of the particles decrease to less than 50 nm for 15 mol % La_2O_3 content and shows only limited decrease as lanthana increases to 20 mol %.

Considering the hydrolysis reaction responsible for the solid solution formation between lanthana and zirconia particles, it can be stated that at temperature as low as 200° C the equilibrium conditions are suitable to obtain ZrO_2 in the cubic structure with only 4.5 mol % La_2O_3 in its lattice. The intimate contact, in the homogeneous mixture, between the particles of the

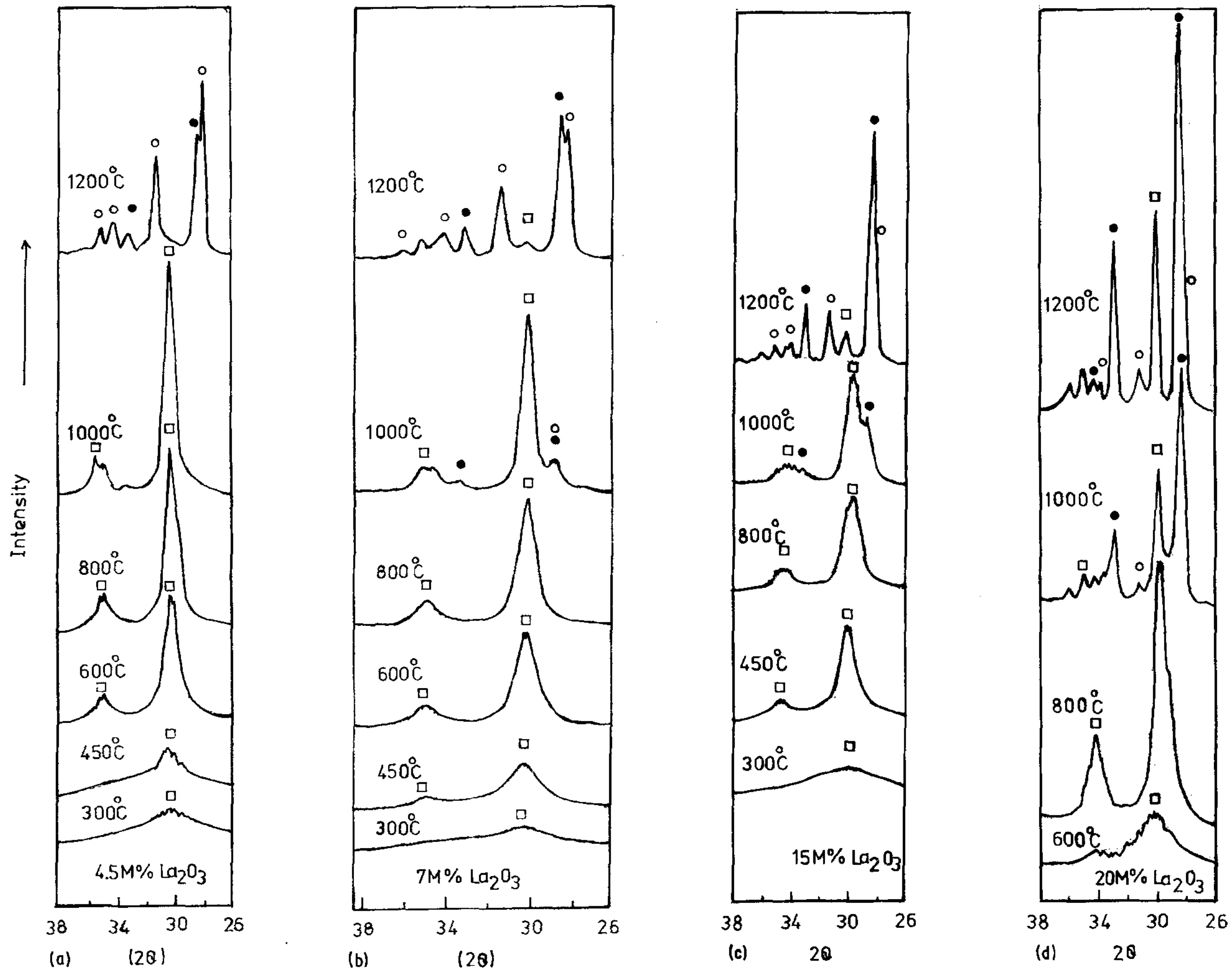

Figure 3 (a–d) X-ray diffraction patterns of the calcined powders. (□) Cubic ZrO_2, (○) monoclinic ZrO_2, (●) La_2O_3.

reactants most probably has helped in reaching to such equilibrium conditions and such very fine powders were obtained.

3.2. The effect of calcination on the prepared powders

X-ray patterns of the calcined materials are shown in Figs 3a to d. From the results it has been found that all the prepared powders remained amorphous to X-ray up to temperatures just below 300° C (up to about 500° C in case of 20 mol % La_2O_3 containing powder). At 300° C a very broad peak extending from $2\theta = 26$ to 38° starts to appear and as the calcination temperature increases up to 800° C this peak sharpens at position of the strongest diffraction line of cubic ZrO_2. At 800° C all the peaks characteristic of the cubic phase are developed reflecting the improvement in the crystallinity of the powders. However, the peaks are diffused and resolved into doublets indicating the still low degree of crystallinity. At 1000° C, the intensity of the cubic phase diffraction lines continues to increase but another phase starts to develop. At this temperature, while no other phases except the cubic ZrO_2 are detected for the 4.5 mol % containing powder, lanthanum zirconate appears in the other patterns in an increasing order as La_2O_3 content increases in the powders. At 1200° C the situation is different; no cubic zirconia phase is detected in the powder containing 4.5 mol % La_2O_3 and instead the pattern shows the characteristic monoclinic ZrO_2 lines together with the lines of lanthanum zirconate. As the La_2O_3 content increases, the cubic ZrO_2 phase continues to remain reaching its maximum at 1200° C for the powder containing 20 mol % La_2O_3. For the same increase in La_2O_3 content, the monoclinic phase decreases noticeably while lanthanum zirconate increases gradually. Taking the ratio of the phases at 1200° C in consideration it is observed that while the cubic zirconia/lanthanum zirconate ratio increases, the monoclinic zirconia/lanthanum zirconate ratio decreases.

The obtained results reveal that the prepared materials are metastable. On heating, the formed zirconia–lanthana solid solutions transform into monoclinic zirconia and the compound $La_2Zr_2O_7$ is formed. The temperature and extent of destabilization of the cubic phase zirconia are dependent on the amount of La_2O_3 in the powder. As La_2O_3 content increases, the cubic phase destabilization is retarded and the amount of the yielded monoclinic phase is reduced. The observed shift in the cubic–monoclinic transformation temperature to higher temperatures as La_2O_3 content increases denotes the continuous nature of the destabilization process. It is believed that during the hydrolysis reaction the relatively large La^{3+} ion (0.115 nm) was able to substitute for Zr^{4+} ion in the crystal lattice of ZrO_2 leading to the observed cubic phase stabilization. As calcination of the powders proceeds to higher temperatures, the conditions are no more suitable for the La^{3+} ion to maintain its position in the cubic structure of ZrO_2 and some sort of splitting

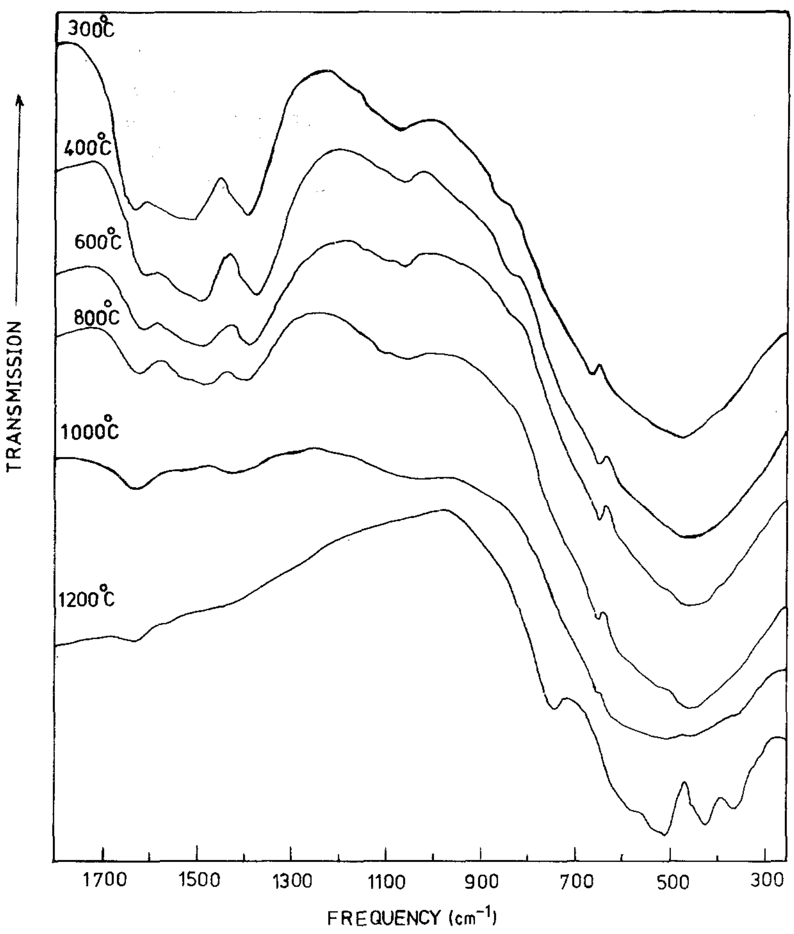

Figure 4 Powder transmission spectra of 15 mol % La_2O_3 containing powder calcined at different temperatures.

took place in the lattice. Despite La_2O_3 was not detected at any stage during calcination, it is believed that La_2O_3 once formed in an active state it reacts with the finely divided ZrO_2 to form the larger $La_2Zr_2O_7$ compound. As the amount of La_2O_3 incorporated in the ZrO_2 lattice increases, more thermal energy is required to cause the lattice splitting. This may explain the continuous shift of complete destabilization to higher temperatures as La_2O_3 content increases.

The above mentioned conclusion has been confirmed by the results of IR measurements as a function of calcination. Fig. 4 shows the infrared spectra of 15 mol % containing powder at different calcination temperatures. As the temperature increases to 800° C, the broad characteristic band (600 to 400 cm^{-1}) of the cubic phase better develops in shape reflecting the improvement in the crystallinity of the powders. At 1000° C, the band starts to lose its well defined shape. The band maximum at $\sim$480 cm^{-1} flattens and weak bands at about 360, 450 and 500 cm^{-1} are hesitating to develop. According to X-ray analysis the cubic phase destabilization has already started at 1000° C. The increase in calcination temperature is accompanied by reduction in the IR bands corresponding to adsorbed H_2O and CO_2 (Section 3.1) and they are eliminated at 1200° C. At this latter temperature the spectrum exhibits group of bands at 360, 420, 510, 575 and 740 cm^{-1}. Similar spectrum was obtained by Phillipi and Mazdiyasni [22] for strained monoclinic ZrO_2 obtained by heating a metastable cubic phase at 766° C for 24 h. They ascribed the strain to the alteration in crystal symmetry of zirconia on heating. The strain-free monoclinic phase displays sharper and additional bands spectra. The characteristic frequencies of the monoclinic phase are readily detected even at low concentrations in a mixed-phase zirconia sample, while the cubic phase can not easily be distinguished

TABLE I Measured densitites (g cm^{-3}) of the bodies fired at different temperatures for 2 h soaking

Firing temperature (° C)	La_2O_3 concentration				
	4.5	7.0	10.0	15.0	20.0
800	2.85	2.77	2.81	2.99	3.19
1000	2.91	2.85	3.05	3.26	3.42
1200	4.31	4.24	4.17	4.20	4.36
1400	5.08	5.24	5.13	5.04	5.01

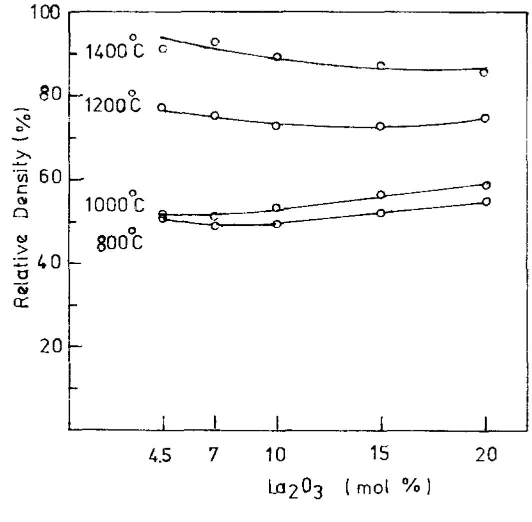

Figure 5 Relative densities of the different bodies fired at the indicated temperatures.

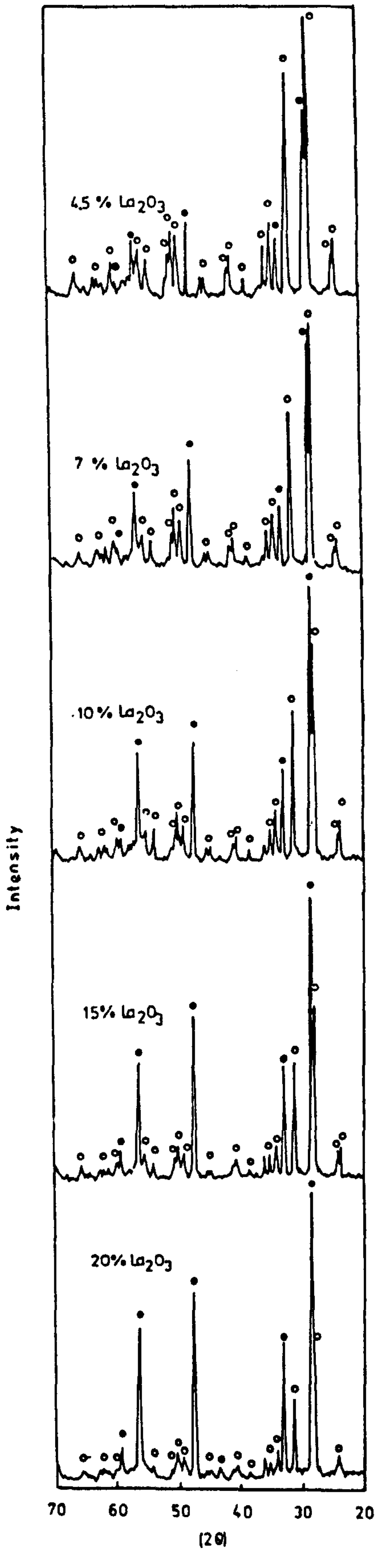

Figure 6 X-ray diffraction patterns of the different bodies fired at 1400° C for 2 h soaking. (○) Monoclinic ZrO_2, (●) $La_2ZR_2O_7$.

due to its broad indistinctive nature [22, 25]. On this basis the disappearance of the cubic phase bands as the destabilization starts can be understood.

3.3. Sintering behaviour

The measured densities of the fired bodies are given in Table I and their percent relative densities are shown in Fig. 5. It can be seen from the data that the sintering behaviour may be divided into two stages. The first one is up to 1000° C where a gradual increase in densities of the bodies is observed with the increase in La_2O_3 content. The second stage is extended between 1200 and 1400° C, where the increase in La_2O_2 content is accompanied by a negative effect in density values.

The reduction of high surface energy in powder compacts is the driving force for sintering during firing [26]. In the previous section it has been shown that up to 1000° C the cubic ZrO_2 solid solutions is the major (if not the only) phase present in the powders. The relative density increases from 52 to 58.6% for bodies fired at 1000° C and containing 4.5 and 20 mol % La_2O_3, respectively. This increase in density could be attributed to the decrease in particle size and agglomeration tendency of the starting powders as La_2O_3 contents increase. The degree of fineness of these powders is considered the dominant factor for sintering in this stage. As the temperature increases to 1200° C, the bodies consist of two or three phases; cubic and monoclinic ZrO_2 as well as lanthanum zirconate. The sintering and crystal growth would proceed differently in the different phases. The X-ray diffraction patterns of the bodies fired at 1400° C are shown in Fig. 6. From the patterns it is evident that the bodies consist of monoclinic ZrO_2 and $La_2Zr_2O_7$ only. The monoclinic ZrO_2/La_2O_7 ratio decreases gradually by the increase of the original La_2O_3 content in the starting powders. A maximum relative density of 92.6% has been reached by firing the body containing 4.5 mol % La_2O_3 and lower values have been obtained for the other bodies. It is assumed that the presence of $La_2Zr_2O_7$ phase in the ZrO_2 matrix could be responsible for reducing the extent of zirconium ion diffusion which operates in eliminating the pores in the body. This assumption may explain the observed arresting of densification as lanthanum zirconate increases in the bodies.

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