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Effect of sintering zirconia with calcia in very low partial pressure of oxygen

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Samples of zirconia containing 0, 8 and 15 mol% calcia were sintered in very low partial pressure of oxygen ($\sim 10^{-6}$ Pa) and the resulting phases, lattice parameters and electrical conductivity studied. The cubic phase was found to be partially stabilized in the calcia-free samples while complete stabilization occurred in the samples containing 8 and 15 mol% calcia. The lattice parameter of the cubic phase showed dependence on the calcia content and the concentration of vacancies at the anion sites. The concentration of these vacancies in the calcia-containing samples is estimated to be 21% and is limited by the appearance of metallic zirconium located in isolated pockets. Electrical conductivity measurements also indicated that the metallic phase was not continually connected. A peak and a minimum in the conductivity–temperature plot are believed to be due to the removal of excess oxygen vacancies introduced during sintering.

1. Introduction

Cubic zirconia stabilized with divalent or trivalent oxides (e.g. CaO, MgO, Y_2O_3) is a non-stoichiometric material with defect fluorite structure, the defect being anion vacancies. For example in the case of calcia-stabilized zirconia a single cubic phase is obtained at about 12 mol% calcia [1], with one oxygen anion vacancy being present for each Ca^{2+} incorporated in the lattice. Before the discovery of the stabilization of zirconia by alloying with oxides, considerable work was carried out on the structure and properties of zirconia sintered or annealed under very low partial pressure of oxygen [2–7]. Such a treatment usually resulted in a body deficient in oxygen, having a black colour and a fairly high concentration of charged defects. Occasionally, some reduction of zirconia to metallic zirconium was also reported, though not confirmed.

All the above effects are expected to be enhanced upon sintering of zirconia containing a cubic-phase stabilizing oxide (e.g. CaO, Y_2O_3, MgO) in the absence of oxygen. In this paper we report some interesting observations, particularly a precipitation of metallic zirconium, upon sintering of some (ZrO_2 + CaO) compositions in a highly oxygen-deficient atmosphere.

2. Experimental details

2.1. Materials and specimen preparation

Samples containing 0, 8 and 15 mol % calcia (denoted henceforth by C_0, C_8 and C_{15} respectively) were prepared using zirconia[†] and calcium carbonate.[‡] The two powders were mixed in the desired ratios, calcined at 1000° C to remove CO_2, pre-sintered at 1800° C for 2 h to homogenize the composition, and after ball milling and pressing into pellets (15 mm diameter) were sintered at 1900° C in a furnace with graphite heating elements in a flowing nitrogen atmosphere. At this temperature the oxygen in the furnace atmosphere combines with the carbon from the heating element, producing carbon monoxide; this lowers the partial pressure of oxygen to below 10^{-6} Pa [8]. All the samples were found to have acquired a black colour after sintereing.

3. Results and discussion

3.1. Phase analysis by X-rays

Table I lists the *d* values corresponding to all the observed X-ray diffraction peaks from the sintered samples; the values from the published sources [9] for all the phases of zirconia which agree most closely with these values are also given. Some of the more prominent peaks are shown in Fig. 1. The C_0 composition contains both the monoclinic and the cubic phases while the C_8 and C_{15} compositions are fully cubic (some tetragonal phase as well as metallic zirconium may also be present as discussed later); in contrast, sintering in air would have led to no stabilization of the cubic phase in the C_0 and only partial stabilization in the C_8 composition [1, 10]. Thus sintering in an oxygen-deficient atmosphere promotes stabilization of the cubic phase.

According to the phase diagram for oxygen-deficient zirconia proposed by Ruh and Garrett [4] no cubic phase is expected to be present at room temperature, even when the oxygen content is as low as

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[†] Indian Rare Earths, Kerala; analysis (wt %): ZrO_2 (ZrO_2 + HfO_2) 99.5, Si 0.1, Fe 0.05, Ti 0.1, (Al + Mg) 0.01.
[‡] Sarabhai M. Chemicals, Baroda; main impurities (wt %): phosphate 0.001, silicate 0.01, Al 0.002, Fe 0.002, Mg 0.01.

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TABLE I X-ray peak intensities and *d* values for C_0, C_8 and C_{15}; matching reference values for pure zirconia [9] are also given

Phase*	*hkl*	From [9]		This work					
		d (nm)	I/I_1	C_0		C_8		C_{15}	
				d (nm)	I/I_1	*d* (nm)	I/I_1	*d* (nm)	I/I_1
M	$1 1 \bar{1}$	0.3157	100	0.3156	100				
T	1 1 1	0.296	100						
C	1 1 1	0.293	100	0.2942	100	0.2954	100	0.2956	100
M	1 1 1	0.2834	65	0.2836	71				
M	0 0 2	0.2617	20	0.2614	26				
C	0 0 2	0.255	25	0.2542	58(C)	0.2558	27	0.2560	26
T	2 0 0	0.254	25						
M	2 0 0	0.2538	14						
M	0 2 1	0.2328	6	0.2318	10				
M	$2 1 \bar{1}$	0.2213	14	0.2206	15				
M	1 1 2	0.2015	8	0.2015	8				
M	$2 0 \bar{2}$	0.1989	8	0.1990	8				
M	0 2 2	0.1845	18	0.1845	20				
T	2 2 0	0.181	35			0.1811	48	0.1814	38
C	2 2 0	1.1801	50	0.1804	70(C)	0.1808	50	0.1811	37
M	$1 2 \bar{2}$	0.1801	12		43(M)				
M	3 0 0, 2 0 2	0.1691	14	0.1695	10				
M	0 1 3, 2 2 1	0.1658	14	0.1653	14				
M	1 3 0	0.1640	8	0.1642	13				
M	$3 1 \bar{1}$, 2 1 2	0.1608	8	0.1609	7				
T	1 3 1	0.1547	45			0.1543	23	0.1545	25
C	3 1 1	0.1534	20	0.1537	39	0.1541	27	0.1543	25
T	2 2 2	0.1493	12			0.1479	23	0.1481	6
C	2 2 2	0.1471	5			0.1475	23	0.1479	6

*M = monoclinic; T = tetragonal; C = cubic.

55 at %. Instead, at 1200° C a mixture of tetragonal zirconia and metallic zirconium is expected below 65 at % oxygen content and only a tetragonal phase for the higher oxygen content (the tetragonal phase would transform to monoclinic on cooling). However, their data were obtained by equilibrating the mixtures of zirconia and zirconium metal at ~ 10^{-3} Pa and the results may not be comparable with the present results.

There is an apparent splitting or broadening of peaks at some of the cubic peak positions, particularly for the (2 2 0), (3 1 1) and (2 2 2) positions in the C_8 and C_{15} compositions (Fig. 1, Table I). This broadening and the extra peaks could not be identified with any of the compounds of calcium, zirconium and/or silicon (as an impurity) for which the X-ray data are available. All the extra peaks occur near the expected peak positions from the tetragonal phase of zirconia; however, the 100% peak at (1 1 1) from the tetragonal phase is not observed. It is possible that this peak, occurring at low angles, overlaps with the (1 1 1) cubic peak since the separation between the peaks becomes appreciable only at the higher angles and tends to increase with the angle (Fig. 1). The presence of the tetragonal phase, therefore, is a strong possibility, especially in the C_8 and C_{15} compositions.

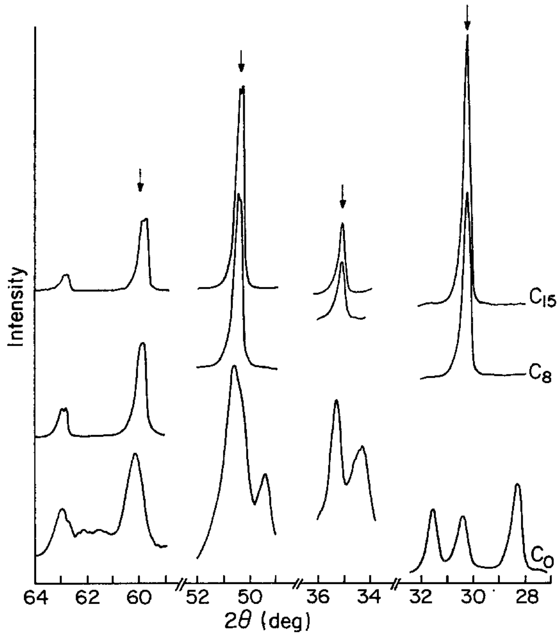

Figure 1 X-ray diffractograms for C_0, C_8 and C_{15} showing the more prominent peaks. Arrows indicate the peak positions for the cubic phase from [9].

The relative amounts of the monoclinic and the cubic phases were determined by the polymorph method [10, 11] in which the stabilized cubic phase is regarded as a high-temperature polymorph of ZrO_2 and the fraction of the monoclinic phase is given by

$$X_m = \frac{I_m(1 1 \bar{1}) + I_m(1 1 1)}{I_m(1 1 \bar{1}) + I_m(1 1 1) + I_c(1 1 1)}$$

where I_m and I_c refer to the intensities of the reflections from the monoclinic and the cubic phases, respectively. Lattice parameters of the cubic phases were obtained from a high-angle plot of the Nelson–Riley function [12].

The amounts and the lattice parameters of the cubic phase for the three compositions are given in Table II. The lattice parameter of C_0 is somewhat lower than the reference value [9] for unalloyed cubic zirconia (0.5091 nm); values for C_8 and C_{15} are larger than this and increase with increasing calcia content. Table II

TABLE II Amount of the cubic phase, its lattice parameter and the concentration of vacant anion sites after sintering and reoxidation

	C_0	C_8	C_{15}
% cubic phase			
After sintering	30	100	100
After reheating 800° C/15 h	30	100	100
After reheating 1350° C/15 h	11	93	96
Lattice parameter of the cubic phase (nm)			
After sintering	0.5087	0.5116	0.5127
After reheating 800° C/15 h	0.5092	0.5117	0.5129
After reheating 1300° C/15 h	*	0.5120	0.5132
% anion sites vacant			
(i) After sintering	–	21	21
(ii) Amount due to sintering alone, obtained after subtracting from (i) the amount due to CaO additions	–	17	13.5
(iii) Amount due to sintering alone as obtained from weight change after reoxidation	–	4	7

*Accurate determination could not be made.

also includes the values of the lattice parameter and the fraction of the two phases obtained after reheating the samples in air at 800 and 1350° C, respectively, for 15 h. There is a destabilization of the cubic phase after the latter treatment. For all compositions, the lattice parameter of the cubic phase increases upon reheating, the increase being larger at the higher reheat temperature.

Anion vacancies are necessarily present in the cubic phase of (zirconia + CaO) after sintering in air ($p_{O_2} \cong 10^5$ Pa). Additional vacancies would be introduced at the anion sites by sintering in a low p_{O_2}. These vacancies are expected to have a negative charge, being different from the uncharged vacancies in a calcia-stabilized, air-sintered zirconia [13]; however, in this paper both types will be referred to as "anion vacancies." Some measurements of the concentration of these vacancies and their effect on the lattice parameter are discussed below, while the effect on electrical conductivity is described later.

As for C_8 and C_{15} – the structure stays almost 100% cubic after the reoxidation at 1350° C – it is possible to calculate the total concentration of anion vacancies from the density (measured separately) and the lattice parameter. Ignoring the presence of the intrinsic vacancies, the excess vacancies introduced due to sintering in low p_{O_2} alone are then arrived at by subtracting the number of vacancies due to the presence of the Ca^{2+} ions. The number of excess vacancies can also be directly obtained by measuring the weight change due to reoxidation and assuming that all of this is due to the introduction of oxygen into the cubic lattice.

The density of the powdered samples was measured using a pycnometer. The weight change on reheating was measured by periodically taking out the sample from the furnace and reheating until there was no further increase in the weight. Details of these measurements are given elsewhere [14].

The results of the calculations of vacancy concentrations in C_8 and C_{15} by the above methods are given in Table II. The total concentration of the anion vacancies in both C_8 and C_{15} after sintering is the same (21%) to within 1%, indicating that this perhaps is the maximum limit that can be accommodated in the cubic lattice. There is a discrepancy in the numbers for the vacancies introduced due to sintering in low p_{O_2} alone, obtained by the subtraction method and by the weight changes. Although some of this can be attributed to the assumption of a 100% cubic phase after reheating, the major part of the difference most probably comes from the presence of a high concentration of intrinsic vacancies, i.e. incomplete reoxidation upon reheating and quenching-in of the vacancies from the reheat temperature.

In view of the above discussion, two factors are likely to influence the lattice parameter in the present case: (i) total concentration of the anion vacancies and (ii) the concentration of Ca^{2+} ions in the cubic phase. An increasing number of anion vacancies leads to a contraction of the lattice while the replacement of Zr^{4+} ions by Ca^{2+} ions, which are about 25% larger, results in an increase in the lattice parameter. As discussed above, sintering in a nearly oxygen-free atmosphere leads to creation of vacancies at the anion sites in addition to those that are already present due to the presence of Ca^{2+}. In C_0, the second effect is absent, so that a lower lattice parameter is observed. In C_8 and C_{15} both the effects are present, but the second effect appears to dominate leading to a net increase in the lattice parameter. In all cases an expansion of the lattice occurs upon reheating in air as the excess anion vacancies are removed, leading to an increase in the lattice parameters.

The increased stability of the cubic phase observed in the present case also appears to be linked to the total concentration of the anion vacancies and can be considered to be a thermodynamic response of the system to the introduction of the additional vacancies by sintering in low p_{O_2}. One can possibly represent the process in terms of a chemical reaction in which the tetragonal phase, the vacancies and the cubic phase "react" according to the reaction

$$\text{defect tetragonal} + \text{vacancies} \rightleftharpoons \text{defect cubic}$$

so that an excess of vacancies, generated by maintaining a low p_{O_2} during sintering, drives the reaction to the right leading to a greater stability of the cubic phase.

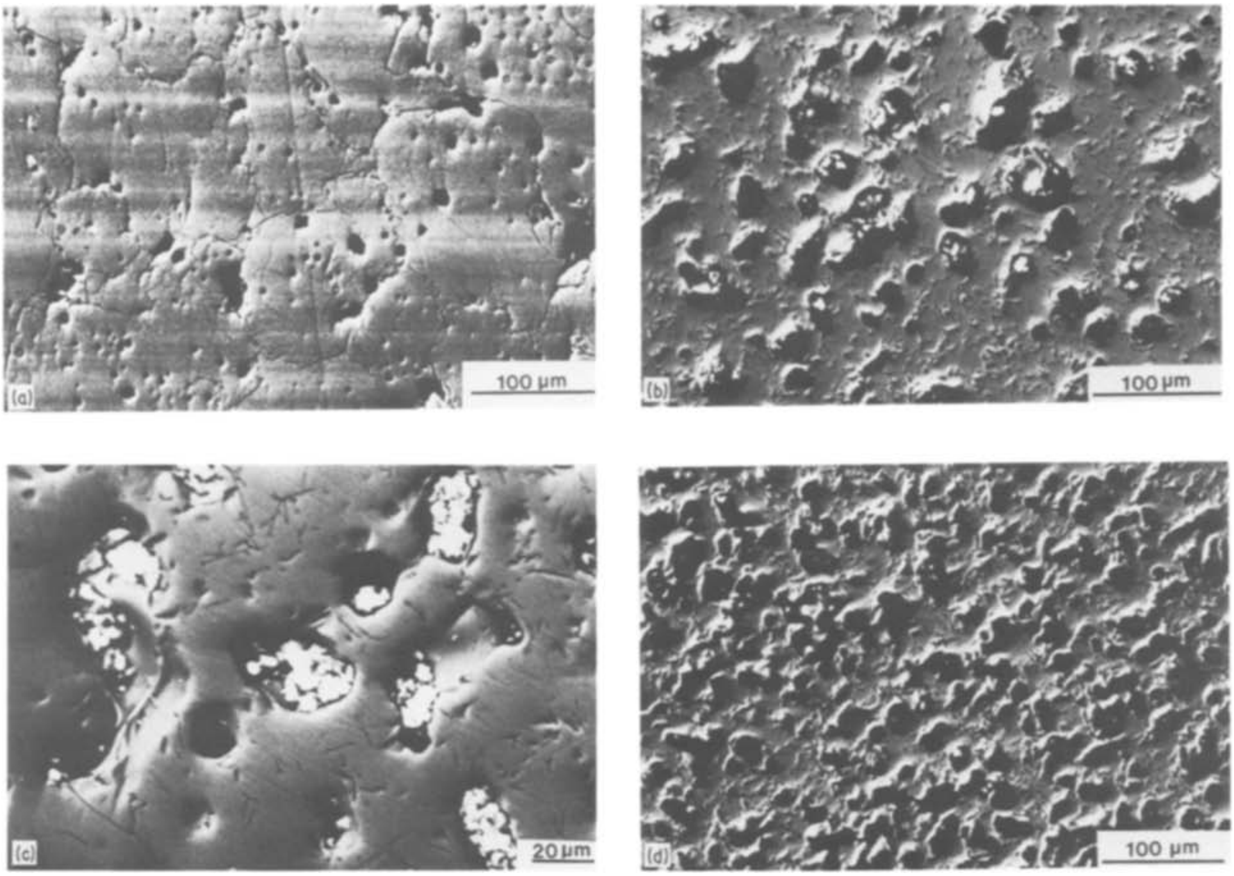

Figure 2 Back-scattered electron images from (a) C_0, (b) and (c) C_8 and (d) C_{15}.

3.2. Electron diffraction and microscopy

Fig. 2 shows the back-scattered electron images from the three types of sample. The C_8 and C_{15} samples contain a granular bright phase in the pores between the grains. It has been reported [4] that in zirconia sintered at 2100° C in a vacuum, the oxygen deficiency is limited by the appearance of a metal phase. It is quite likely therefore that the granular bright phase is metallic zirconium, the bright contrast arising because of its higher zirconium content (100%) than the matrix. The large dihedral angle ($\sim 88°$) between metallic zirconium and ZrO_{2-x} reported by Virkar and Lynn Johnson [15] is expected to lead to just such a morphology. Moreover, electron diffraction carried out on finely powdered samples in an electron microscope produced diffraction patterns (Fig. 3) corresponding to zirconium metal in the case of C_8 and C_{15} (in addition to the diffraction patterns from the cubic phase; in the case of C_0, diffraction patterns from monoclinic and cubic phases only were observed). Thus small amounts (less than $\sim 1\%$, the limit for detection by X-ray diffraction) of metallic zirconium are present in the C_8 and C_{15} compositions. Most likely this appears as the bright granular phase in the microscope. The lack of connectivity of the metallic phase is supported by the electrical conductivity measurements described in the next section.

The limiting oxygen deficiency above which the metallic phase begins to precipitate in our samples can be identified with the maximum concentration of the anion vacancies (21%) in C_8 and C_{15} as described earlier.

3.3. Electrical conductivity measurements

The primary interest in measuring the electrical conductivity was to determine if the metallic phase is distributed discretely or connected continuously. It is generally accepted that the conductivity of zirconia stabilized in the fluorite structure by addition of divalent and trivalent oxides is essentially ionic over a wide range of temperature and that the mobile ions are the anions [16–18]. In the air-sintered material, the

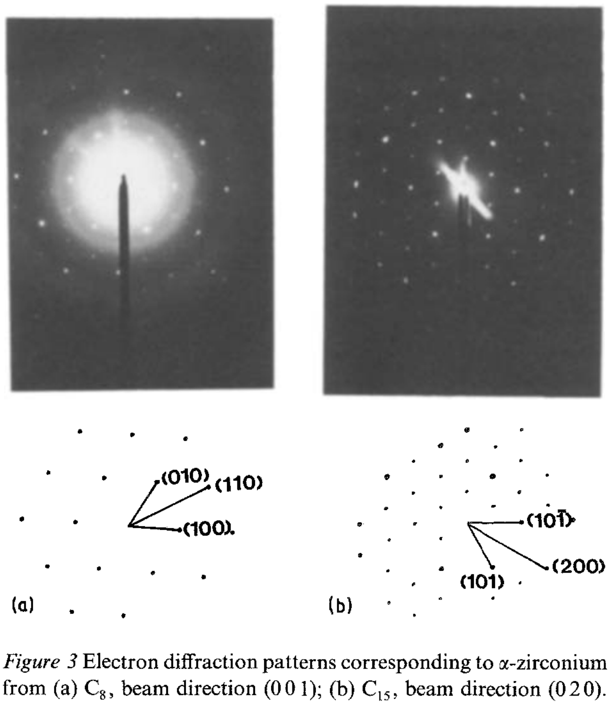

Figure 3 Electron diffraction patterns corresponding to α-zirconium from (a) C_8, beam direction (0 0 1); (b) C_{15}, beam direction (0 2 0).

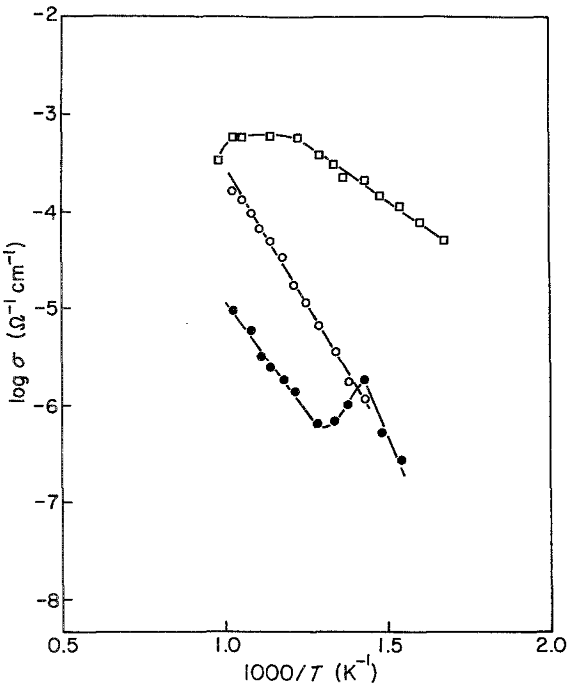

Figure 4 Variation of log (conductivity) with reciprocal temperature for (●) C_0, (□) C_8 and (○) C_{15}.

anion vacancy concentration is fixed by composition – each added molecule of CaO introduces one anion vacancy to restore the charge neutrality disturbed due to the replacement of Zr^{4+} by Ca^{2+}. However, the conductivity does not increase monotonically with CaO addition–maximum conductivity occurs at the lower limit of the single-phase cubic region which is at about 12 mol % calcia for the ZrO_2–CaO system. This behaviour was explained by Tien and Subbarao [16] in terms of the higher activation energy required for an anion to move in the presence of Ca^{2+} ions which are about 25% larger than the Zr^{4+} ions which they replace. This, coupled with the fact that the fraction of the monoclinic phase, which has a lower conductivity than the cubic phase, decreases as CaO content increases, gives rise to a maximum in conductivity. In the present case, where the samples have been sintered in a highly oxygen-deficient atmosphere, some additional effects may be expected because of the presence of excess vacancies and other defects.

Electrical conductivity of the samples was measured at 1 kHz between 250 and 700° C in air using a General Radio 1608 impedance bridge. Platinum electrodes were fused to silver lead wires and were spring-loaded. The sample was held for 20 min at each temperature before making the measurement. Fig. 4 shows the variation of log (conductivity) with $1/T$ for the three samples.

The low conductivity values support the microscope observations that the metallic zirconium in the C_8 and C_{15} samples is distributed discretely and does not form a continuous network.

It is seen that, at all temperautres, the conductivity first increases with the initial addition of CaO to 8 mol % and is lowered when the CaO content is further increased to 15%. This result is in agreement with the results for the air-sintered materials in the literature as discussed above.

A remarkable feature of the present results is the presence of a peak and a minimum in conductivity plots for the C_0 and C_8 compositions. The temperature of the peak is higher and the peak is broader for C_8 than for C_0. It is possible that a peak in C_{15} would also have been observed if the measurements could have been extended to higher temperatures.

In separate measurements, no change in the amounts of monoclinic and cubic phases was observed upon reheating the samples in air at 800° C for many hours; however, the lattice parameter of the cubic phase increased slightly (Table II), all the samples changed in colour from black to white and their weight increased. These results rule out the possibility of the peaks in the conductivity of C_0 and C_8 samples occurring due to any phase changes. The changes in the lattice parameter, weight and colour are most probably due to the removal of some, if not all, of the excess anion vacancies introduced during sintering. A similar change in colour is also observed in the samples after the conductivity measurements.

A complete discussion of the electrical conductivity results obtained here must recognize the presence of defects other than anion vacancies [13] and examine their contribution to the total conductivity. However, if it is assumed that the dominant conduction mechanism is still the anion conduction, as is the case for air-sintered zirconia containing calcia, yttria or scandia [19], then a simple explanation of the observed results would be that the removal of the excess anion vacancies due to heating in air during the conductivity measurements results in a decrease in conductivity by reducing the diffusivity of the anions, thus producing a peak in the conductivity. After the minimum, the vacancy removal, if still occurring, is more than compensated due to the increased diffusivity at higher temperatures. This explanation could also account for the increase in the peak temperature with the amount of calcia, and for the increased width of the peak. Thus the diffusion of the anion vacancies will be more difficult as the number of calcium ions increases, as discussed earlier [16]. This would cause the temperature of the peak, which corresponds to the temperature for removal of excess vacancies, to increase with increasing calcia content as observed. Moreover, the binding energy of the anion vacancy in the lattice will tend to have a wide distribution when calcium ions are present because a vacancy can now have as its neighbours the zirconium and calcium ions in varying ratios. This distribution in the binding energy would become broader as the CaO content is increased, thereby producing a broader conductivity peak.

The activation energies calculated using the low-temperature data (before the peak) from Fig. 4 are 16.9, 4.6 and 10.6 kcal mol^{-1} (70.8, 19.3 and 44.4 kJ mol^{-1}) for the C_0, C_8 and C_{15} compositions, respectively. These values are much lower than the 24.5 to 29.1 kcal mol^{-1} (102.6 to 121.8 kJ mol^{-1}) reported for zirconia with 12 to 15 mol % calcia, sintered in air [16, 20, 21]. This is expected in view of the excess vacancies in our material if the conduction is predominantly by the anions. The value for C_8 lies between C_0 and C_{15}, which also agrees with such a mechanism.

4. Summary

Sintering of zirconia and zirconia with 8 and 15 mol % calcia in a low partial pressure ($\sim 10^{-6}$ Pa) of oxygen results in the following:

1. Partial stabilization of the cubic phase occurs even in the calcia-free zirconia samples, while in the sample containing only 8 mol % calcia the stabilization is complete–full stabilization can probably be obtained with less than 8% CaO. The enhanced stabilization can be viewed as the thermodynamic response of the system to the need for accommodating a large number of anion vacancies introduced during sintering.

2. The lattice parameter of the cubic phase increases on increasing the calcia content between 0 and 15 mol %. There is a further increase upon reheating the samples in air at 800 and 1350° C. The former effect can be attributed to the larger (by ~25%) size of Ca^{2+} as compared to Zr^{4+}, and the latter to the removal of the anion vacancies from the cubic lattice. Higher temperature (1350° C) treatment also results in a destabilization of the cubic phase.

3. Electron diffraction reveals the presence of metallic zirconium in the 8 and 15 mol % CaO composition; this appears in isolated pockets between the grains. These compositions also have an equal (and maximum) concentration of the vacant anion sites (21%) after sintering. It is proposed that this represents the maximum fraction of vacant sites that can be accommodated in the cubic lattice. Beyond this, precipitation of metallic zirconium takes place.

4. A peak occurs in the plot of electrical conductivity against $1/T$ for 0 and 8 mol % calcia samples. The temperature of the peak increases upon addition of calcia; perhaps a peak would have also been observed for the 15 mol % calcia if the measurements could have been extended beyond 700° C, the highest attained in our apparatus. The occurrence of the peak is attributed to the removal of anion vacancies upon reheating in air during the conductivity measurements.

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