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EFFECT OF STOICHIOMETRIC COMPOSITIONS ON THE DEVELOPMENT OF PHASE AND MICROSTRUCTURE IN CALCIA STABILIZED ZIRCONIA CERAMIC

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Calcia stabilized zirconia (CSZ) ceramic material was synthesized with stoichiometric compositions 4, 8, 12 and 16wt.% by mixed oxide reaction using fine homogeneous salts of zirconia and calcia. Powder compacts were sintered at 1950°C for 6h in an inert argon atmosphere. The phase identification, purity, crystalline and lattice parameters of cubic CSZ were measured by X-ray diffraction (XRD). Combination of cubic zirconia ($Ca_{0.15}Zr_{0.85}O_{1.85}$), calcium-zirconium oxide ($CaZrO_3$) and zirconium oxide (ZrO) phases were observed in all compositions. The percent relative densities were measured in order to evaluate the material performance and found to decrease from 85 to 74% with increase of stoichiometeric compositions 4 to 16wt%. These results were in agreement with scanning electron microscopy (SEM) where it was observed that porosity increased with increase of calcia. The co-efficient of thermal expansion was estimated by dilatometry. The results revealed that coefficient of thermal expansion (α) decreases with the increase of compositions from 4 to 16wt.% .

Keywords: Calcia stabilized zirconia, Microstructure, XRD, Dilatometry, Ceramic

1. Introduction

Zirconia ceramics have many fascinating properties such as high mechanical strength and high fracture toughness. Fully stabilized and partially stabilized zirconia can be obtained by introducing di- or tri-valent oxides, such as CaO, MgO, Sc_2O and Y_2O_3. These systems have traditionally received most attention as solid electrolyte membranes in electrochemical devices, like oxygen sensors, solid oxide fuel cells [1-3]. Physico-mechanical properties of fully and partially calcia or yttria stabilized zirconia have been greatly studied and various reviews are available [4-6]. Several synthesis methods have been commonly used for the preparation of fully or partially calcia or yttria stabilized zirconia (CSZ or YSZ). The homogenous composition, micro and nanosized grains of CSZ or YSZ have been observed in all these methods [7-18]. It has been shown [19-20] that a cubic solid solution rich in zirconia can be formed by firing the oxide with certain other refractory oxides and that, in some cases, this cubic form is stable at high temperature. The formation of a stable cubic form can be accomplished most effectively by the addition of (a) 11.5 to 15% of Y_2O_3 and heating at 1700°C or higher (b) 8 to 15% of MgO and heating at 1500^oC or higher (c) 5 to 15% of CaO and heating at 1500^oC or higher respectively. Addition of CaO is most widely used commercially, not only because CaO is cheap but also because the cubic form remains stable at all temperatures whereas the MgO and Y_2O_3 stabilized forms may revert to the monoclinic structure at low temperatures [21-22]. Thermal conductivity of solid zirconia with specific gravity of 4-4.4 is very low and can be decreased further by increasing porosity and this low thermal conductivity shared with low specific heat reassure and low heat storage. These properties make CSZ ideal material in which heat conservation at high temperature is very important. CSZ is an excellent insulation material with moderately good thermal-shock resistance for construction of high temperature furnaces. Some important data have been found in literature about the sintering of calcia and yttria stabilized zirconia ceramics at $1400\text{-}1700^oC$ in air [23-25].

The current work deals in the study of the effect of calcia doping on development of cubic phase and microstructure of calcia stabilized zirconia ceramics sintered at high temperature (1950°C) in

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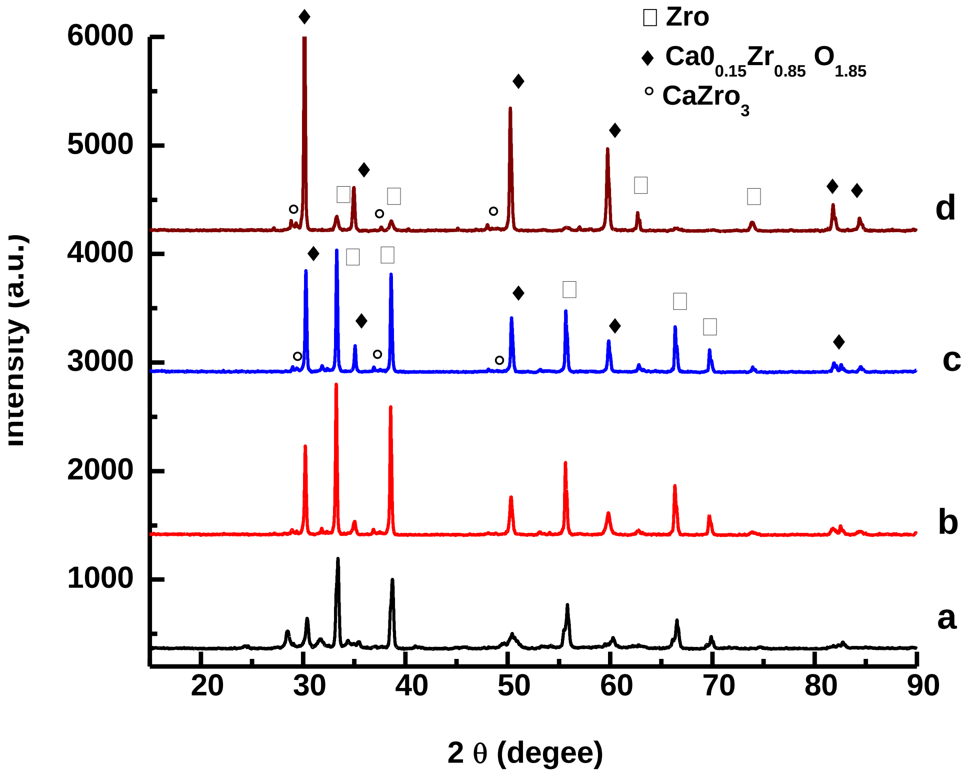

Figure 1(a-d). X-ray diffraction pattern (a) 4CSZ, (b) 8CSZ, (c) 12CSZ and (d) 16CSZ.

an inert medium. The variation in sintered densities, mechanism of phase transformation, microstructure changes and thermal expansion co-efficient of CSZ ceramic was also ascertained. The current work constitutes a part of our ongoing studies on calcia stabilized zirconia (CSZ) and the results are based on the techniques previously applied [12].

2. Experimental

Calcia stabilized zirconia (CSZ) ceramic was prepared in different compositions i.e. 4, 8 12, 16 wt.% calcia. Specimens were designated as 4CSZ, 8CSZ, 12CSZ & 16CSZ respectively. High purity chemicals, calcium oxide (Fluka) and zirconium oxide (Merck) were mixed using ball mill for 5h and then calcined at 900°C for 1h. The calcined powders were ground and then pressed into green pellets (17.8mm diameter and 3-4mm thickness) by uni-axial hydraulic press of load capacity 216MPa using 2% polyvinyl alcohol (PVA) as binder. The binder is burned out by heating at 400-500°C for 2h. The heating rate was $0.1Ks^{-1}$ to avoid cracking of pellets. The green pellets were sintered at 1950°C in argon atmosphere for 6h time intervals in resistance heating furnace with variation of temperature ±2°C. Density of CSZ specimens was measured using Ultra Pycnometer 1000 (Quantachrome) and verified by Archimedes buoyancy method. The phase analysis and crystal structure was measured by X-ray diffraction on a DMAX-IIIC Rigaku instrument with CuK_{α} (λ =1.5418 A°) radiation. The XRD data were recorded in 2θ range from $15^{o}<2\theta<80°$ by step scanning 0.05^{o} increments. Coefficient of thermal expansion was observed on horizontal high temperature computer-controlled differential dilatometer (NETZSCH, DIL 409) with heating rate of 10°C/min upto 1100°C/min in static air. Microstructural features of CSZ were observed by SEM (LEO 4401). The sintered pellets were placed on aluminum stud and then coated via thin layer of gold sputtering.

3. Results and Discussion

3.1. X-Ray Diffraction

Figure 1 (a-d) illustrate the X-ray diffraction (XRD) patterns of samples 4, 8, 12 and 16wt% calcia stabilized zirconia (CSZ) sintered at 1950°C for 6h in argon atmosphere. The spectra show

Table 1. X-ray diffraction characteristics of calcia stabilized zirconia.

Sample	Percentage of phases				Symmetry of Particle	Unit cell parameter (Å)	Cell volume $(Å)^3$	Space group
	ZrO	ZrO_2	$CaZrO_3$	$Ca_{0.15}Zr_{0.85}O_{1.85}$				
4CSZ	63	14	2	20	Cubic	5.135	135.40	Fm 3^{-} m
8CSZ	57	-	2	36	Cubic			
12CSZ	52	2	3	40	Cubic			
16CSZ	4	2	7	87	Cubic			

the presence of ZrO and $Ca_{0.15}Zr_{0.85}O_{1.85}$ phases in all the samples. However, in sample 16CSZ, a new phase $CaZrO_3$ is also observed in conjunction with aforementioned phases. Lee and Agli et al. [26, 27] found in their study that $CaZrO_3$ formed at intermediate stage i.e., around 1000°C and above 1100°C becomes weaker and its decreased amount was the indication of transition from tetragonal to cubic phase. In the current investigation, the presence of small amount of $CaZrO_3$ phase in 16 weight percent CSZ (Fig. 1d) showed that this phase could not totally decompose in the intermediate stage.

The phases identified alongwith their percentages by XRD with increasing amount of calcia are given in Table 1. The highest volume fraction of cubic phase $Ca_{0.15}Zr_{0.85}O_{1.85}$ can be observed in 16CSZ, which indicates that maximum amount of phases such as ZrO and $CaZrO_3$ have transformed into single cubic phase. It is assumed that the presence of large amount of $CaZrO_3$ at the lower temperature helps to increase the volume fraction of $Ca_{0.15}Zr_{0.85}O_{1.85}$ at higher temperature, so the addition of 16wt.% calcia is more suitable to obtain the higher volume fraction of desire phase i.e. $Ca_{0.15}Zr_{0.85}O_{1.85}$.

XRD data is also analyzed to determine the symmetry of particle, unit cell parameters, cell volume and space group and these values are presented in Table 1. The results revealed that XRD patterns and unit cell parameters are well matched with reported values of JCPDS cards (ZrO; 51-1149 and $Ca_{0.15}Zr_{0.85}O_{1.85}$; 26-341) which confirms that the prepared CSZ is cubic crystalline material [28].

3.2 Micro Structural and Physico-chemical Properties

Figure 2 (a-d) shows the SEM microstructure of samples of 4CSZ, 8CSZ, 12CSZ and 16CSZ sintered at 1950°C for 6h in an inert gas atmosphere. It can be observed that the porosity increases with the addition of calcia. These results are in agreement with the measurement of density as given in Table 2. It was observed [29] that the presence of calcia as a second phase led to poorer densification and responsible for the presence of open porosity in the sintered samples. In the present investigation, it can be assumed that the enhanced %age of calcia has played a vital role in decreasing the sintered density. Present results also predicted that the sample 16CSZ seems to be more suitable as a lining material for high temperature furnaces because the presence of high %age of porosity compared to other samples (4CSZ, 8CSZ and 12CSZ).

The physico-chemical properties of sintered samples 4, 8, 12 and 16CSZ are given in Table 2. The relative densities (after sintering at 1950^oC) of CSZ were found to decrease (85-74%) with the increase of stoichiometeric compositions 4 to 16wt% of calcia. These values are in agreement with the microstructure analyzed by SEM already shown in Figure 2 (a-d), where a high fraction of porosity can be observed in 16CSZ sample i.e., low density.

The bulk porosity for each sample was also calculated from the relative density by using the following equation:

Bulk Porosity (%) = 100 – Relative Density (%)

The values of bulk porosity (%) are also shown in Table 2. These are also in agreement with microstructures observed by SEM.

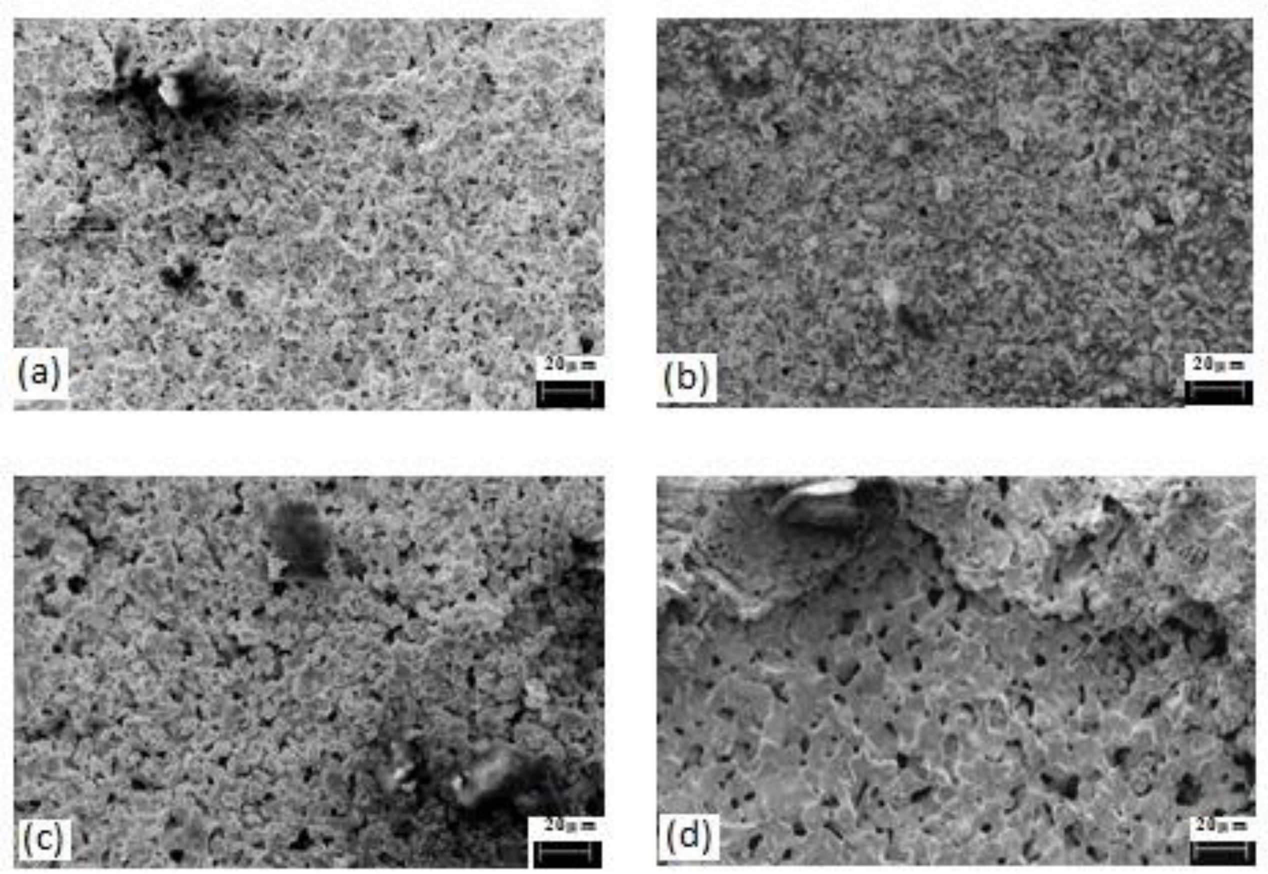

Figure 2(a-d). SEM microstructures of calcia stabilized zirconia with (a) 4CSD (b) 8CSD, (c) 12CSD and (d) 16CSD.

Table 2. Sintering characteristics of calcia stabilized zirconia.

Sample	Theoretical density (g.cm^{-3})	Sintered density (g.cm^{-3})	Relative density (%)	Bulk Porosity (%)
4CSZ	5.586	4.767	85.34	14.66
8CSZ	5.493	4.602	83.74	16.26
12CSZ	5.399	4.225	78.25	21.75
16CSZ	5.305	3.974	73.53	26.47

3.3. Co-efficient of Thermal Expansion

Figure 3 (a-d) shows the coefficient of thermal expansion (CTE, $\alpha = \mathrm{x}10^{-6}\ ^\circ\mathrm{C}^{-1}$) measured using a dilatometer at 1000^{o}C in air for samples 4, 8, 12 and 16 CSZ; the values are 7.159, 6.223, 5.988 and 5.366 x $10^{-6}\ ^\circ\mathrm{C}^{-1}$ respectively. The result revealed that α decrease with increase of composition from 4 to 16wt.% calcia. The value of CTE also indicated that the bond strength of 16CSZ sample is more in comparison to others due to higher volume fractions of cubic phase $Ca_{0.15}Zr_{0.85}O_{1.85}$. Dudek et al. [29] also observed that $CaZrO_3$ based ceramics exhibited lower thermal expansion coefficients than that of zirconia solid electrolytes and concluded that it has better resistance to thermal shock in operating conditions involving temperature fluctuations.

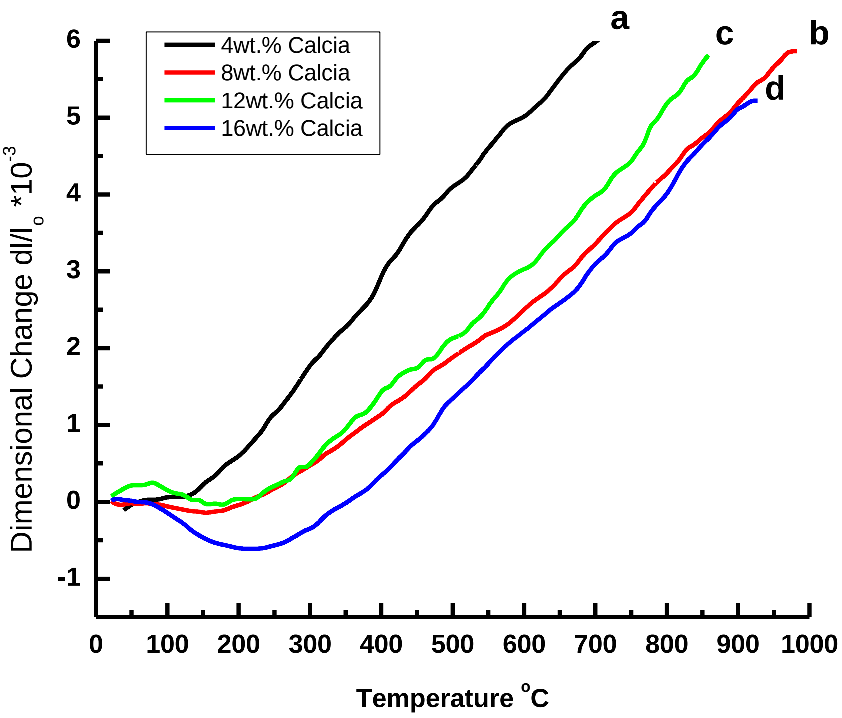

Figure 3 (a-c). Dilatometric curves of calcia stabilized zirconia (a) 4CSZ (b) 8CSZ (c) 12CSZ and (d) 16CSZ.

4. Conclusions

Calcia stabilized zirconia compacts were sintered at 1950°C for 6h in an inert gas atmosphere and found that relative densities of CSZ samples were decreased (85-73%) with the increase of stoichiometeric compositions (4-16wt.% calcia). High volume fraction of desired phase ($Ca_{0.15}Zr_{0.85}O_{1.85}$) was observed in 16 weight percent CSZ sample. Scanning electron microscopy results revealed that 16CSZ sample is more porous as compared to others. The coefficient of thermal expansion decreased with the increase of composition from 4 to 16wt.% and showed that bond strength of 16CSZ sample is more in comparison to others because of higher volume fractions of cubic phase $Ca_{0.15}Zr_{0.85}O_{1.85}$.

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