CHAPTER IV

EVALUATION OF MECHANICAL BEHAVIOR

4.1 INTRODUCTION

Evaluation of mechanical properties of the sintered samples is an important step for considering the ceramic materials as components for engineering, structural and functional devices. The analysis of the mechanical behavior gives an idea about the reliability of the components. A better mechanical property can be achieved by proper optimization of the powder processing, grain growth and homogeneity of the microstructure. Better sintered samples possess better mechanical properties. As demand increases for the materials which possess good mechanical properties with relatively lesser cost, new processing and fabricating methods are explored to meet out the requirements.

The subject discussion of this chapter is a brief outline of various mechanical properties, methodology adopted for the evaluation of mechanical properties of the sintered samples and the results obtained from the experiments.

4.2 BRIEF DISCUSSION ABOUT THE VARIOUS MECHANICAL PROPERTIES

4.2.1 Hardness

Hardness of a material is its resistance to indentation by an indenter whose hardness is higher than the hardness of the material. It may be termed as a measure of the resistance against lattice destruction or the
resistance offered to permanent deformation or damage. An important use
of the hardness studies is the possibility of making indirect estimate on
other mechanical properties of materials having a specific correlation with
hardness. As the hardness properties are basically related to the crystal
structure and the bond strength, hardness studies can be applied to
understand the plasticity of the particular material. It is a technique in
which a crystal is subjected to relatively high pressures within a localized
area. By suitable choice of the indenter material and relatively simple
equipment construction, hardness test can be easily applied to all crystalline
materials under various conditions of temperature and environment. Since
the deformation is local, a number of tests can be made on a single specimen
of small dimensions and can be reproduced by maintaining the specimen flat
with relatively smooth surface.

Hardness measurements can be carried out by various methods. They are classified as follows:

1. Static indentation test
2. Dynamic indentation test
3. Scratch test
4. Rebound test
5. Abrasion test

The most popular and simplest one is the static indentation test
wherein an indenter of specific geometry is pressed onto the surface of a test
specimen under a known load. The indenter may be a ball or diamond cone
or diamond pyramid. The static indentation method was followed by Brinell,
Meyer, Vickers, Knoop and Rockwell test (Tabor 1951; Neil 1967; Wyatt and
Hughes 1974).

Among the various methods of hardness measurements, the most
common and reliable method is the Vicker's hardness test. In this method,
indentation is made on the surface of a specimen with the help of diamond pyramidal indenter. Hardness is generally defined as the ratio of the load applied to the surface area of the indentation. The Vicker's hardness number $H_v$ or DPN (Diamond Pyramid Number) is defined as

$$H_v = \frac{2F \sin (\theta/2)}{R^2}$$

where $\theta$ is the apex angle of the indenter ($\theta = 136^\circ$). The Vicker's hardness number is therefore calculated from the relation

$$H_v = 1.8544 \frac{F}{R^2} \text{ Kg/mm}^2$$

where $F$ is the applied load in Kg and $R$ is the diagonal length of the indentation mark in mm. Hardness values are always measured from the observed size of the impression mark after making indentations on the surface for different loads. Thus the observed hardness behavior is the summation of a number of effects involved in the material's response to the indentation pressure during loading and which is the final measurement of the residual impression.

4.2.2 Fracture toughness

Toughness is a measure of energy which is used for initiation and propagation of a crack in the material. The fracture toughness or critical stress intensity factor ($K_{IC}$) can be considered as one of the most important fracture properties of structural ceramic materials. Different methods are used to determine this property. However, it may be classified into two types (Lai et al 1989)

1. Vicker's indentation methods
2. Conventional methods - single edge notched beam (SENB), chevron notched beam (CVNB) and double cantilever beam (DCB)

4.2.2.1 Vickers indentation method


Though there exists many expressions to calculate the fracture toughness, no universal formula is available to evaluate the exact values of $K_{IC}$ using any crack profile produced over a large range of loads, for any ceramic material. Based on the type of cracks developed around the indentation impression, various expressions are used. However, the popular and widely used equation for the measurement of fracture toughness is developed by Niihara et al. (1982) and is given as follows:

$$K_c = 0.0711 \left( \frac{H_v}{g} \right)^{1/2} (E/H_v)^{2/5} \left( \frac{c}{g} \right)^{3/2}$$  \hspace{1cm} (4.3)

where
- $H_v$ is Vicker's hardness
- $E$ is the Young's modulus
- $g$ is the half diagonal length of indentation
- $c$ is the half-crack length

4.2.2.2 Conventional beam fracture toughness techniques

Many reviews exist (Evans 1974; Shih and Opoku 1979; Lai et al. 1989) in which almost all the methods are described to evaluate the fracture toughness of a material. Out of the several available techniques on fracture toughness, only two methods are described here namely, single edged notched beam (SENB) and chevron notched beam (CVNB) techniques.
SENB technique normally used for metals, is based on BS 5447:1977 (1977) or ASTM Standard testing method E-399 (1983). Even though the testing methods can usually be applied to metal samples, the terminology, definitions and testing techniques are applied to ceramic materials also (Brinkies 1989). This technique (Evans 1974; 1976; Shih and Opoku 1979) is a simple and easy method to use under different environments and temperatures, because it uses compressive loads. The specimen, however, requires a very delicate wedge loading precracking procedure. $K_{IC}$ strongly depends on the notch width and notch radius of the specimen. It can be loaded in a three or four point configuration. There are several precracking methods available fatigue precracking, thermal shock precracking, wedge precracking, etc. But for ceramics, their application is not satisfactory (Shih and Opoku 1979; Brinkies 1989).

In the CVNB or short rod/bar technique, the specimen consists of a rod/bar with a diameter equal to 2/3 of its length and longitudinal slots which form an internal V-shaped region. The major advantages of this method are its simplicity and inexpensive test sample and further it does not require measurements of crack length separately. The V notch has been introduced in the bar by diamond saw cut. This technique is most widely used (Heusser and Claussen 1989).

4.2.3 Flexural strength

The evaluation of strength of a material is an essential criteria for structural applications and is considered as an important design parameter. Normally, for ceramic materials tensile, compression and bend tests are widely used. Many factors like defects, fracture toughness and Young's modulus are the parameters to decide the strength of a ceramic material. The measuring techniques also influence the strength of a material. Creyke et al (1982) listed a number of factors which normally have influence on the measured strength values by various methods. For example, the effect of
size of a specimen on strength is a key parameter; the larger the specimen, the greater is the volume under test and the lower is the average value of strength. There is no international standard for the determination of the flexural strength for ceramic materials. However, U.S. Department of Army (1990) has developed a standard for the flexural strength of ceramics at ambient temperature. The other existing flexural strength test standards are listed by Loveday and Morrell (1989).

4.2.4 Weibull modulus and strength

For reliability analysis on a set of data of strength, there are number of statistical functions available (Davidge 1979). Strength variation and reliability analysis of ceramic materials are determined by a function used by Weibull (1951).

According to Weibull, the probability of failure, \( P_s \), can be defined as

\[
P_s = \frac{i}{N+1}
\]

(4.4)

for the \( i \)-th ranked sample in a group containing \( N \) number of samples. Further, it is seen that a plot of \( \ln(\ln(1/P_s)) \) versus \( \ln(\sigma) \) gives a straight line with a slope "\( m \)" called Weibull modulus. The values of \( m \) in the range of 5-20 are common for ceramics.

4.3 EARLIER WORK ON THE MECHANICAL PROPERTIES

Tsukuma (1986) and Tsukuma and Shimada (1985) have analyzed the behavior of mechanical properties of ceria-tetragonal zirconia polycrystals for a wide range of compositions prepared by precipitation method. They have showed that the Vickers hardness, ranging from 650 to
1150 $H_v$ depends on the composition, grain size and the amount of $t\rightarrow m$
phase transformation during indentation. Annamalai et al (1993) have
observed that the Vicker's hardness value for the sintered sample with 12
mole% of Ce-TZP which retains 100% $t$ phase, is 882 $H_v$. For 10 mole% of
Ce-TZP electro-refined powders, Hepworth and Pindar (1987) and Chen and
Brook (1989) have reported a range of values from 870 to 1003 $H_v$ depending
on the sintering schedule.

The bending strength of Ce-TZP strongly depends on both
composition and the sintering temperature. For example, Hepworth and
Pindar (1987) have noticed that the dense samples of 10 mole% of $\text{CeO}_2$-TZP
gave 701 MPa, for a firing temperature of 1350°C whereas for the same
composition fired at 1500°C gave only 574 MPa. Tsukuma et al (1988) have
analyzed the dependency of bend strength on grain size of the sintered
sample and composition. Sato et al (1993; 1994) have reported the bending
strength of 12 mole% of $\text{CeO}_2$-$\text{ZrO}_2$ crystallized in various medium and
sintered at different temperatures.

Fracture toughness values as high as 30 MPam$^{1/2}$ have been
reported (Hannink 1988). Vicker's indentation method (Tsukuma and
et al 1989) Chevron notched beam technique (Tsukuma and Shimada 1985;
Tsukuma et al 1988; Heusser and Claussen 1989), and Single edge notched
beam method (Bar-on et al 1990; Annamalai 1992; Ponraj 1993) are widely
used to determine $K_{IC}$. It is very difficult to produce cracks around the
indentation mark by using Vicker's diamond indenter. Many workers (Duh
et al 1988a; Heusser and Claussen 1989) have noted the absence of cracks
around the indentation mark on the Ce-TZP materials. Fracture toughness
is also influenced by composition, sintering temperature and grain size of
the samples. As discussed in Chapter I, the three important properties, viz.,
bending strength, hardness and fracture toughness cannot be improved
individually.
Gupta et al (1977) have first reported the fully tetragonal zirconia polycrystals by the addition of 3 mole% of Y$_2$O$_3$ with zirconia sintered at less than 1500°C and the bend strength for the sintered samples. Since then many reports have been published on the mechanical properties of this class of materials. Lange (1982b) has done extensive work on the transformation toughening due to the stress induced $t\rightarrow m$ phase transformation and the contribution to the fracture toughness for various composition of Y$_2$O$_3$-ZrO$_2$ ceramics. Effect of high pressure on the fracture toughness was reported by Noma et al (1988b) stating that the toughness increases with increase of pressure. Tsukuma et al (1988) have studied the variation of fracture toughness with respect to the composition of yttria and retention of cubic phase. They found that 3 mole% of Y$_2$O$_3$ has higher fracture toughness value, 17 MPam$^{1/2}$, for HIPed samples. Chen and Brook (1989) have reported that the fracture toughness value for conventionally sintered 3Y-TZP samples is 8 MPam$^{1/2}$. Cutler et al (1992) have reported toughness values of different composition of Y$_2$O$_3$-zirconia samples either CIPed and then sintered or HIPed directly.

Hardness value of HIPed Y-TZP samples as high as 13 GPa has been reported by Tsukuma et al (1988). For the electro-refined powder of 3.2 mole% of Y-TZP, 1392 MPa has been noticed (Hepworth and Pindar 1987). For this, the powders were isostatically pressed followed by conventional sintering. Noma et al (1988b) have analyzed the effect of high pressure on the hardness behavior of Y-TZP. They found that the hardness value initially increases with pressure and temperature and then decreases. Chen and Brook (1989) have reported the hardness value of 13.3 GPa for both electro-refined and the co-precipitated powders.

Bending strength value as high as 1800 MPa has been reported for Y-TZP fabricated by hot pressing method (Masaki and Kobayashi 1988). Gupta et al (1977) have studied the bending strength of Y-TZP with different compositions. Tsukuma et al (1988) have observed the strength of
2.5 GPa for 3 mole% of HIPed Y-TZP sample with moderate fracture toughness. Flexural strength has a wide range of values with respect to yttria composition and the method of fabrication (Hannink 1988). Sato et al (1994) have reported the strength of 3Y-TZP materials crystallized in organic solvents and subsequently sintered by conventional method.

In order to improve the bending strength of the Ce-TZP, Duh et al (1988a; 1989) have fabricated the Y-Ce-TZP materials with different composition by coprecipitation technique using ZrOCl$_2$.8H$_2$O, Ce(NO)$_3$.6H$_2$O and Y(NO$_3$)$_3$.5H$_2$O as parent materials. By the addition of yttria to the Ce-TZP, the grain growth of Ce-TZP is greatly inhibited which thereby tends to reduce the transformation temperature, since a decrease in grain size decreases the transformation temperature from t→m phase (Lange 1982c; Heuer et al 1986; Becher 1986; Garvie and Goss 1986). Another advantage of this ternary system is the inhibition of low temperature degradation of Y-TZP ceramic material. A review article explains on the low temperature degradation of Y-TZP (Hirano 1992).

Duh et al (1988a) have discussed the various mechanical properties like hardness, bending strength and fracture toughness with respect to different compositions, grain size, sintering temperature and soaking time for the ternary system Y-Ce-TZP material. Urabe et al (1988) have reported the fracture toughness and strength of 4CeO$_2$.4Y$_{0.5}$.92ZrO$_2$ system. Toughness of fully sintered (Y,Ce)-TZP has been studied by Boutz et al (1995). They have concluded that there is no explicit variation of toughness with grain size.

4.4 SCOPE OF THE PROBLEM

As discussed so far, the availability of data for the mechanical properties of 10 mole% of CeO$_2$-ZrO$_2$ is limited. The chemically derived powder shows crack during sintering for this particular composition and
hence could not be studied. However, the mechanical properties for this composition of Ce-TZP have been derived from electro-refined technique and reported (Hepworth and Pindar 1987; Chen and Brook 1989). The reports on mechanical properties of 5 mole% of Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> is also limited. As far as author's knowledge is concerned, there is no report available on 4 mole% of Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> material. Hence in this work, the mechanical properties such as Vicker's hardness, fracture toughness (SENB and CVNB methods) and bend strength of 10 mole% of CeO<sub>2</sub>-ZrO<sub>2</sub>, 5 mole% of Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and 4 mole% of Y<sub>2</sub>O<sub>3</sub>-7 mole% of CeO<sub>2</sub>-ZrO<sub>2</sub> samples derived from oxalate gel have been evaluated.

4.5 EXPERIMENTAL PROCEDURE

4.5.1 Hardness

Vicker's indentation method was used to determine the hardness of the samples. Circular pellets of dia 10mm were uniaxially pressed at 240 MPa using a single acting cold uniaxial press (experimental procedure is common for all the samples, namely, 10 mole% of CeO<sub>2</sub>-ZrO<sub>2</sub>, 5 mole% of Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> and 4 mole% of Y<sub>2</sub>O<sub>3</sub>-7 mole% of CeO<sub>2</sub>-ZrO<sub>2</sub>). Hardness was calculated using computerized Zwick hardness tester (Germany). The standard expression for the determination of hardness has already been given.

The hardness was calculated for two diagonal lengths separately and the average values are reported here. Atleast five such measurements were made and the average values were reported. Optical photograph (Figure 4.1) shows a typical indentation mark for Ce-TZP sample. For the Ce-TZP samples, 10 kg load was applied to produce the indentation marks on the surface of the samples and for other samples it was 2 Kg. The indentation impression was made on the as-sintered surfaces of the samples.
Figure 4.1  Optical photograph of a typical indentation mark on the surface of a ACZ sample

Figure 4.2  Photograph of the green notched samples. 
  a = CVNB and b = SENB
4.5.2 Fracture toughness

Two different methods, SENB and CVNB techniques, were used to calculate the fracture toughness of the samples. Dense rectangular bars of size 4.5 mm x 3.5 mm x 32 mm were made by using single acting cold uniaxial press at 240 MPa. Considering the difficulties encountered during the preparation of notch using diamond saw cutter on the sintered samples, the notches were made on the green samples itself based on the works of Annamalai (1992) and Ponraj (1993). Diamond indentation technique was not used to evaluate the toughness due to the difficulty in producing the cracks around the indentation mark and the reliability of the value.

In this work, a razor blade was used to make a notch in the pressed sample before firing. After sintering, by regular schedule, fracture toughness was calculated by breaking the samples in the three point bending mode. More details about this method of notch preparation are presented in the results and discussion section. For this, Zwick Universal testing machine (Germany) was used. Optical photograph (Figure 4.2) shows some of the sintered SENB and CVNB samples with razor blade notch. Figures 4.3 and 4.4 show the schematic diagram of SENB and CVNB samples.

Notched beams were sintered and subjected to three point bending mode in order to determine the failure load. Average values of five samples were reported. From the failure load, the following expression was used to calculate the fracture toughness of SENB samples (Elssner 1990).

\[
K_{Ic} = \frac{3 F (L/2) a^{1/2}}{B W^2 Y_k} 
\]  

(4.5)
Figure 4.3 Schematic of the SENB sample.
Figure 4.4 Schematic of the CVNB sample.
Where

\[ \begin{align*}
F &= \text{force required to break the SENB samples in 3-point bending} \\
L/2 &= \text{distance between loading and supporting points} \\
a &= \text{depth of the notch} \\
B &= \text{thickness of the specimen} \\
W &= \text{width of the specimen} \\
Y_k &= \text{shape factor}
\end{align*} \]

For three point bending,

\[ Y_k = 1.96 - 2.75(a/W) + 13.66(a/W)^2 - 23.98(a/W)^3 + 25.22(a/W)^4 \] (4.6)

The fracture toughness for the CVNB samples was calculated using the relationship (used by Orange et al 1987),

\[ K_{IC} = \frac{F_{\text{max}} L}{B W^{3/2}} \left( 3.08 + 5\alpha_o + 8.33\alpha_o^2 \right) \left( \frac{\alpha_1 - \alpha_o}{1 - \alpha_o} \right) \] (4.7)

Where

\[ \begin{align*}
F_{\text{max}} &= \text{force required to break the CVNB samples in 3-point bending mode} \\
L &= \text{distance between loading and supporting points} \\
B &= \text{thickness of the specimen} \\
W &= \text{width of the specimen} \\
\alpha_o &= \frac{a_o}{W} \\
a_o &= \text{distance between the edge of the wedge and surface of the sample} \\
\alpha_1 &= \frac{a_1}{W} \\
a_1 &= \text{height of the wedge shaped notch}
\end{align*} \]
4.5.3 Flexural strength

Three point bending test was carried out to estimate the flexural strength of the fabricated dense rectangular bars of size 3.5 mm x 4.5 mm x 32 mm with a span length of 20 mm. Samples were fabricated using a single acting uniaxial cold press at 240 MPa. Rectangular hardened steel die was used for this experiment. Three point bending tests were conducted using an Universal testing machine (Zwick, Germany) at a strain rate of 0.5 mm/min. From the failure loads, the bending strength was calculated.

Statistical analysis of bend test results was carried out by plotting the failure probability against the bending strength of 20 samples. The Weibull modulus (m) was obtained from the slope of the straight line of such Weibull plot (Morrell 1985). As established in the sintering schedules, two temperatures were chosen, 1400 and 1500°C for the fabrication of dense sintered bodies to evaluate the mechanical properties. Since slow heating rate gives better results than the fast heating rate, slow heating rate was chosen for this study.

Powder X-ray diffraction patterns were recorded for the sintered as well as the broken samples to ascertain the phases present. SEM photographs were recorded for the broken surface to analyze the fracture morphology.

4.6 RESULTS AND DISCUSSION
4.6.1 Hardness

It is observed from the Table 4.1 that the hardness values of the CZ and ACZ samples vary from 6.9 to 7.6 GPa for grain size value around 2μ and also shows that the hardness value decreases with increase of sintering temperature. The hardness values for CZ samples are lower than the ACZ samples which may be due to the heterogeneity in packing while
sintering. The decrease of hardness with increase of temperature may be explained as follows. As the sintering temperature increases, the grain size also increases. According to the grain size effect, for \( t \rightarrow m \) phase transformation, larger the grain size, easier the transformation. As the sintering temperature and soaking period increase, the grain size also increases. During indentation, the larger size grains transform easily from \( t \rightarrow m \) phase and hence the decrease in hardness values. Tsukuma and Shimada (1985) have also reported that the hardness value decreases with increase of grain size and decrease of CeO\(_2\) content. While indentation is made on the samples, more percentage of \( t \rightarrow m \) transformation occurs which results in lower hardness value. Chen and Brook (1989) have also reported a hardness value of 8.7 GPa for 10 mole% of Ce-TZP samples prepared from electro-refined powders.

Table 4.1

<table>
<thead>
<tr>
<th>Fired Temp. °C</th>
<th>Soaking period hours</th>
<th>Samples</th>
<th>Cz</th>
<th>ACZ</th>
<th>YZ</th>
<th>AYZ</th>
<th>YCZ</th>
<th>AYCZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>3</td>
<td>Cz</td>
<td>6.9</td>
<td>7.3</td>
<td>8.5</td>
<td>10.48</td>
<td>9.12</td>
<td>9.65</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>ACZ</td>
<td>6.5</td>
<td>7.15</td>
<td>7.7</td>
<td>9.98</td>
<td>8.7</td>
<td>10.54</td>
</tr>
<tr>
<td>1400</td>
<td>3</td>
<td>YZ</td>
<td>--</td>
<td>7.64</td>
<td>--</td>
<td>10.98</td>
<td>--</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>AYZ</td>
<td>--</td>
<td>7.25</td>
<td>--</td>
<td>10.11</td>
<td>--</td>
<td>10.12</td>
</tr>
</tbody>
</table>

Hardness values of YZ and AYZ samples vary from 10.98 to 7.7 GPa for grain size value around 0.8 \( \mu \) which are shown in Table 4.1. Generally the hardness value of yttria stabilized zirconia is higher than the Ce-stabilized zirconia. The following are the reasons for the higher hardness values for this system. Smaller grain size and composition are major reasons for this family of materials apart from the fabrication methods. The stability of the \( t \)-phase increases with the composition which restricts the \( t \rightarrow m \) phase
transformation. Cutler et al (1992) have reported 13.7 GPa for the hot pressed 6 mole% of Y-ZrO₂ samples. For this composition, the observed phase is cubic and hence there is no chance of phase transformation during indentation which results in higher hardness values. Further, it is clear from the Table 4.1 that the hardness values for the AYZ samples are higher than that of the YZ samples. The observed difference in the hardness may be due to the difference in the powder homogeneity which is always one of the predominant deciding factor of the final properties.

Table 4.1 shows the hardness values of YCZ and AYCZ samples sintered at different temperatures and soaking periods. The observed hardness values range from 9.12 to 10.54 GPa for a grain size value around 0.7 μ. It can be seen that the hardness values increase with increase in sintering temperature and soaking periods which are attributed to the increase in density. The observed trend is in agreement with the results of Duh et al (1988a). The partial substitution of Y₂O₃ in the binary system CeO₂-ZrO₂ increases the hardness value. The observed higher hardness value may be due to the stability of the t phase while indentation is made on the sample. As observed for the binary systems, in this ternary system also, the powder processing method influences the hardness value. The hardness values for the AYCZ samples are higher than the YCZ samples which may be due to homogeneity of the AYCZ samples.

Comparison of these three systems shows that the hardness value decreases for the binary system with increase in sintering temperature, whereas it increases for the ternary system. The reason for the increase of hardness value for the ternary system may be due to the increase of density with sintering temperature.
4.6.2 Fracture toughness

For the consideration of the engineering design aspects, the evaluation of fracture toughness of a material is an important criteria. Normally, two methods are used to determine the fracture toughness, namely, indentation and single edge notched beam (SENB) methods. It has already been reported that there is a difficulty in producing visible/measurable cracks around the indentation loads at 490 N (Duh et al 1988a), 300 N (Blackburn et al 1988b) and even at 1000 N (Heussner and Claussen 1989). Although Tsukuma (1986) has reported about visible cracks of short length developed around the indentation at a load of 490 N, this method can be considered only to show the trend of toughness of Ce-TZP materials.

By considering the difficulties in producing the crack around the indentation, in the present work, two methods have been used to measure the fracture toughness, namely, single edge notched beam (SENB) and chevron notched beam (CVNB) techniques.

Since indentation techniques are not reliable (considered to be only 30% accurate as reported by Morrell 1985), notched beam techniques (Morrell 1985) are often used. Machine notching on sintered body can induce stress as well as cracks, the effect of which cannot be completely nullified by annealing and the fracture toughness estimation for transformation toughening of materials therefore do not yield realistic values. Hence, in the present work, a method developed by Annamalai (1992) and Ponraj (1993) has been used to prepare notch on the green samples itself. The notch preparation technique is briefly described here. The available thinnest tool was the razor blade (0.12mm thick) which was used as notching tool. In order to improve the effectiveness of the cutting, the cutting edge of the razor was formed to a saw tooth shape by filling it with a diamond coated hand file. By holding the pressed green compacts in one hand, the prepared
razor edge was used gently like a saw and the notch was prepared. Notches could be prepared to any predetermined $a/w$ ratio ($a$ - precrack depth and $w$ - specimen depth) and these specimens are then sintered at the desired temperature.

In addition to the problems arising during the notch preparation using diamond saw as reported by Annamalai et al. (1993), there are also other problems which exist in the green stage notch preparation (Andreas Krell 1994). According to Andreas Krell, during green stage notching, the pressure exerted by the razor blade produces difference in local green density of the ceramic microstructure immediately beneath and on both sides of the cutting edge. In order to reduce these effects, care must be taken during the green notching of the samples.

Similar technique was also used to prepare the CVNB notch. Notches could be prepared to any desired $a_1/w$ and $a_2/w$ ratios. The notches prepared by this method were very sharp and after sintering, only $t$ phase was observed for the samples and no $m$ phase was observed. This type of notch preparation technique was used for all the samples.

Tables 4.2 and 4.3 show the fracture toughness values of CZ and ACZ samples with sintering schedules. It varies from 6.5 to 7.4 MPam$^{1/2}$ for SENB and 6 to 7.1 MPam$^{1/2}$ for CVNB samples with respect to the various sintering temperatures and preparation methods. For the dry milled samples, the toughness values are lower than the wet milled samples. Ponraj (1993) has reported the value of 5 MPam$^{1/2}$ for 12 mole% of Ce-TZP (Tosho, Japan) samples which was measured by three point bend test with SENB notch whereas in this work a toughness value of as high as 7.4 MPam$^{1/2}$ has been observed for sol-gel derived 10 mole% of Ce-TZP which may be due to the variation of composition as well as powder processing route. For 10 mole% of Ce-TZP, Chen and Brook (1989) have reported 16 MPam$^{1/2}$ by four point bend method with the CVNB notch, which was made
Table 4.2

$K_{IC}$ (in MPam$^{1/2}$) of the SENB samples sintered at different conditions for a fixed a/w (a/w = 0.25) ratio

<table>
<thead>
<tr>
<th>Fired Temp. °C</th>
<th>Soaking period hours</th>
<th>Samples CZ</th>
<th>ACZ</th>
<th>YZ</th>
<th>AYZ</th>
<th>YCZ</th>
<th>AYCZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>3</td>
<td>6.5</td>
<td>7.4</td>
<td>4.0</td>
<td>4.32</td>
<td>4.1</td>
<td>5.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>7.0</td>
<td>7.1</td>
<td>3.8</td>
<td>5.01</td>
<td>4.5</td>
<td>5.4</td>
</tr>
<tr>
<td>1400</td>
<td>3</td>
<td>--</td>
<td>7.0</td>
<td>--</td>
<td>4.5</td>
<td>--</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>--</td>
<td>7.4</td>
<td>--</td>
<td>5.1</td>
<td>--</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Table 4.3

$K_{IC}$ (in MPam$^{1/2}$) of the CVNB samples sintered at different conditions for a fixed a$_{o}$/w (0.02) and a$_{t}$/w (0.35) ratios

<table>
<thead>
<tr>
<th>Fired Temp. °C</th>
<th>Soaking period hours</th>
<th>Samples CZ</th>
<th>ACZ</th>
<th>YZ</th>
<th>AYZ</th>
<th>YCZ</th>
<th>AYCZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>3</td>
<td>6.0</td>
<td>6.1</td>
<td>4.0</td>
<td>4.52</td>
<td>4.0</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>6.0</td>
<td>6.0</td>
<td>4.0</td>
<td>5.0</td>
<td>5.0</td>
<td>5.1</td>
</tr>
<tr>
<td>1400</td>
<td>3</td>
<td>--</td>
<td>6.0</td>
<td>--</td>
<td>4.3</td>
<td>--</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>--</td>
<td>7.1</td>
<td>--</td>
<td>4.8</td>
<td>--</td>
<td>5.0</td>
</tr>
</tbody>
</table>
on the sintered body. Tsukuma and Shimada (1985) have reported around 9 MPam$^{1/2}$ for 11 mole% of Ce-TZP using the CVNB notch and they found that there was not much influence of the t→m phase transformation on toughness. In this work, the highest observed value for the Ce-TZP material is 7.1 MPam$^{1/2}$ which clearly shows the difference in the notch preparation techniques. However, the value obtained in the present work is higher than that of the value (6 MPam$^{1/2}$) reported by Tsukuma et al (1988). Further Tsukuma has prepared the notch on the sintered samples which definitely could not yield the more reliable fracture toughness value as discussed by Ponraj (1993). It is attributed to the combination of the actual t→m transformation, residual stress and microcracks due to grinding by diamond wheel. Whereas in the present work there is no question of other effects on fracture toughness which depends only on the t→m transformation and the inherent material property. The calculated volume fraction of m phase for the fractured surface shows 38 volume percent.

Tsukuma (1986) reported a highest value of fracture toughness for 12 mole% of Ce-TZP as 40 MPam$^{1/2}$ with 1.5 μ grain size by indentation method and concluded that the increase of grain size can increase the toughness. But using the three or four point bend test with SENB or CVNB notches, it may not be possible to obtain this much of value because the former one is due to plastic deformation resulting from stress-induced transformation while the latter is related to initiation of crack rather than the crack propagation (Tsukuma and Shimada 1985). Sato et al (1989) have showed that the K$_{fc}$ of Ce-TZP can also be improved to 22 MPam$^{1/2}$ from 15 MPam$^{1/2}$ by HIPing in an 80 volume % Ar - 20 volume% of O$_2$ gas atmosphere. By using CIPing followed by sintering, the K$_{fc}$ can also be improved to certain extent.

It is seen from the Tables 4.2 and 4.3 that the fracture toughness values of 5 mole% of Y-TZP varied from 3.8 to 5.1 MPam$^{1/2}$ for SENB samples and 4 to 5.0 MPam$^{1/2}$ for CVNB samples sintered at various
conditions. The differences in fracture toughness for the different samples are due to the sintering and processing conditions. Lange (1982c) has reported the fracture toughness value of 4.5 MPam$^{1/2}$ for conventionally sintered 5 mole% of Y$_2$O$_3$-ZrO$_2$ samples, which was evaluated by indentation method on the finely polished surface. Recently, Gokhale *et al* (1994) have reported the fracture toughness for the Y-TZP materials. They observed that the fracture toughness varies with respect to the composition, crystallite size, phase content and fabrication methods. For 5Y-TZP, they reported the value of around 3 MPam$^{1/2}$ and a highest value for 2 mole% of Y-TZP with 100% t phase as 6.5 MPam$^{1/2}$. They have also reported that the toughness decreases with increase of Y$_2$O$_3$ content and also due to the increase of cubic phase content and the volume percent of non-transformable t phase. Masaki and Kobayashi (1988) have reviewed various mechanical properties of PSZ (Partially Stabilized Zirconia). They have also reported a similar trend but the value of fracture toughness is as high as 20 MPam$^{1/2}$ for HIPed 2 mole% of Y-TZP material and the fracture toughness decreases with the increase of yttria content irrespective of the fabrication route.

As far as the fracture toughness is concerned, the fabrication techniques like HIP, HP and CIP have less influence on the samples containing higher content of yttria in the zirconia system. For example above 3 mole% of yttria (Refer Figure 1.15), there is not much of a variation.

Comparing the results of the present work with this, the conventional uniaxially pressed samples followed by sintering show comparable value of fracture toughness which is obtained for the samples processed by advanced techniques like HIP, etc. The fracture toughness values obtained, in this work, are evaluated with SENB and CVNB notches by breaking the samples in the three point bend mode. Also the notches are prepared in the green stage itself and hence the values of $K_{IC}$ are purely related to crack initiation. If the notch is prepared on the sintered samples, the value may be still higher due to crack deflection by the microcracks.
during breaking. Since the volume of the transformable tetragonal zirconia (TTZ) phase decreased sharply for the 5 mole% of yttria-zirconia (Gokhale et al 1994), the fracture toughness also decreased considerably. The calculated volume fraction of monoclinic phase on the fractured surface is 12 volume percent.

Fracture toughness values of YCZ and AYCZ are shown in Tables 4.2 and 4.3. It can be seen that the $K_{IC}$ values varies from 4.1 to 5.4 MPam$^{1/2}$ for the SENB notched samples and 4 to 5.5 MPam$^{1/2}$ for the CVNB notched samples. Again the variation in fracture toughness is attributed to the sintering time, temperature and the sample homogeneity. Urabe et al (1988) have reported 7.96 MPam$^{1/2}$ for $4(\text{Y-Ce})_2\text{ZrO}_2$ samples which are CIPed followed by sintering at 1600°C for 20 hrs and the $K_{IC}$ has been determined by notched beam technique. Duh et al (1988a) have shown that the addition of $\text{Y}_2\text{O}_3$ to the 12 mole% of $\text{CeO}_2$ reduces the fracture toughness. For example, addition of 1 mole% of $\text{Y}_2\text{O}_3$ to 12 mole% of $\text{CeO}_2$-89 mole% of $\text{ZrO}_2$ yields the $K_{IC}$ as 15 MPam$^{1/2}$ whereas 2 mole% of yttria to 12 mole% of $\text{CeO}_2$-88 mole% of $\text{ZrO}_2$ gives only 5 MPam$^{1/2}$, and the $K_{IC}$ values were measured by indentation technique. The $K_{IC}$ values obtained in the present work with notched beam technique is comparable to that of the values obtained by Duh et al. The value 7.96 MPam$^{1/2}$ reported by Urabe et al (1988) may not be a more reliable value since, they have prepared the notch on the sintered samples, whereas in the present work the obtained value is only due to $t\rightarrow m$ transformation and material property. Recently, Boutz et al (1995) have extensively studied the effect of yttria doping with Ce-TZP on fracture toughness. They showed that the composition dependency of $K_{IC}$ values. The observed decrease in toughness value may be due to the stability of the $t$ phase during fracture. The observed volume fraction of $m$ phase for the fractured surface is 9 percent.
From these observations, in the present work, it is to be noted that the contribution of t→m phase transformation on fracture toughness values is very much lesser for the yttria containing samples, whereas for Ce-TZP is more and hence the $K_{IC}$ value is also more for Ce-TZP.

From the Table 4.7 it is clear that the increase of yttria content with 12 mole% of CeO$_2$-ZrO$_2$ decreases the fracture toughness and the increase of ceria content keeping yttria content constant (4 mole% of yttria-zirconia) also decreases the toughness. Hence, to obtain maximum value of fracture toughness, there may be an optimum composition of codopants lying in the region of 1-3 mole% of Y$_2$O$_3$ and 10-14 mole% of CeO$_2$ content with the zirconia system.

Comparing these three systems, namely, 10 mole% of CeO$_2$-ZrO$_2$, 5 mole% of Y$_2$O$_2$-ZrO$_2$ and 4 mole% of Y$_2$O$_3$-7 mole% of CeO$_2$-ZrO$_2$, the Ce-TZP system has the highest toughness value which agrees well with the reported literature. The observed lower values for other systems may be due to the stability of t phase.

4.6.3 Weibull modulus and bending strength

As given in the Table 4.4, the bending strength of CZ and ACZ samples vary from 200 to 301 MPa depending on the sample homogeneity, sintering temperature and soaking period. Table 4.4 shows the average values obtained during three point bend tests. Tsukuma (1986) has reported that the fracture strength of 10 mole% of CeO$_2$-ZrO$_2$ containing small amount of (La,Nd)$_2$Zr$_2$O$_7$ is 450 MPa which was sintered in a temperature range from 1450 to 1600°C. For the electro-refined samples, Chen and Brook (1989) have reported the bending strength value for Ce-TZP as 470 MPa. As compared with these values, the bending strength value of the present work is lower. The reason may be due to the low final density of the samples. In this work, only 97-98% of TD has been achieved. The bending
strength can be increased further by improving the density. The SEM photograph for the fractured surface of ACZ sample is shown in Figure 4.5a. It is seen from the figure that the fracture mode is inter-granular type. From this, the homogeneity of the sinterability is noticed.

Table 4.4

Bending strength (in MPa) of the samples sintered at different conditions

<table>
<thead>
<tr>
<th>Fired Temp. °C</th>
<th>Soaking Period hours</th>
<th>Samples CZ ACZ YZ AYZ YCZ AYCZ Weibull modulus CZ YZ YCZ ACZ AYZ AYCZ</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>3</td>
<td>219 245 296 330 284 374</td>
<td>4.67 5.17 - - - -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>200 227 277 312 296 400</td>
<td>- - 5.66 - - 15.43</td>
</tr>
<tr>
<td>1400</td>
<td>3</td>
<td>- 301 - 371 - 341</td>
<td>- - - 14.13 17.13 -</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>- 262 - 343 - 358</td>
<td>- - - - - -</td>
</tr>
</tbody>
</table>

From the Table 4.4 it is also seen that the bending strength decreases with increase of soaking period and temperature. For the ACZ samples, the highest bending strength has been obtained for a soaking period of 3 hrs at 1400°C. However, Tsukuma and his co-workers (1986, 1988) have also reported the bending strength for 12 mole% of CeO₂-ZrO₂ samples, in the range 225 - 240 MPa.

Bending strength of 5 mole% of Y₂O₃-ZrO₂ samples are given in the Table 4.4. These values vary from 277 to 371 MPa depending on the sintering temperature, soaking period and powder processing conditions. The powder processing step has a marked influence on the final strength of the sintered samples. Due to the homogeneity and soft agglomeration
Figure 4.5  Fracture surface of the wet milled samples sintered at 1400°C.
  a = ACZ; b = AYZ and c = AYCZ
  d = YZ (dry milled sample sintered at 1500°C)
nature, the wet milled samples have better strength than the dry milled samples. It is to be noted that the strength is not much influenced due to the variation in soaking periods at a particular sintering temperature. This may be correlated with the final sintered density of samples in which there is no significant variation and hence the bending strength. The SEM photograph of the fracture surface of AYZ and YZ are shown in Figures 4.5b and 4.5d. A smooth transgranular fracture surface is observed. The observed fracture mode agrees with the result of Lange (1982b). Lange has explained that this type of smooth fracture surface is due to the different fracture topographies of t and c phases of zirconia. In the fracture surface of YZ sample, the existing porosity is high due to the powder inhomogeneity.

The bending strength of 4.5 mole% of Y$_2$O$_3$-ZrO$_2$ samples has been reported to be 450 MPa by Masaki and Kobayashi (1988). In this case the samples have been CIPed followed by sintering. Recently Gokhale et al (1994) have determined the bending strength of 5Y-TZP as around 280 MPa for the conventionally sintered sol-gel derived samples. For this composition they have found that the value of the transformable t phase is sharply decreased and hence the observed value of strength is lower. Also they observed that the bending strength varies depending on the yttria composition, phase content and fabrication methods. Cutler et al (1992) have reported the bending strength value as 350 MPa, for the 6 mole% of Y$_2$O$_3$-ZrO$_2$ samples which are HIPed. In this work, for 5 mole% of Y$_2$O$_3$-ZrO$_2$ samples, it has been observed that the bending strength value is 371 MPa which is comparable to the reported values.

Bending strength of the AYCZ and YCZ samples is given in Table 4.4. The values vary from 284 to 400 MPa depending on the sintering temperature, soaking period and the powder processing method. Fracture strength values obtained for the wet milled samples are higher than the dry milled powders which reflects the homogeneity and sinterability of the wet milled powders. As far as the author's knowledge is concerned there is no
report available for this composition. Figure 4.5c shows the fracture surface of the AYCZ sample. For this sample also, the transgranular fracture mode is observed. This fracture surface is similar to that of AYZ sample. Table 4.7 shows the bending strength for various compositions. It can be seen from the table that the bending strength decreases with increase in the ceria content at a constant yttria composition. For example, the strength of (2.5Y-4Ce)-ZrO₂ is 1000 MPa whereas for (2.5Y-5.5Ce)-ZrO₂ it is 860 MPa. Similarly, keeping the ceria content constant and increasing yttria content also decreases the bending strength. For example the bending strength of (4Y-4Ce)-ZrO₂ is 840 MPa whereas, for (4Y-7Ce)-ZrO₂ it is 400 MPa. Although the phase diagram (Figure 1.12) shows that there is a wide range of composition which are suitable for structural applications, only a few compositions give better mechanical properties.

In order to verify the reliability of the samples, Weibull modulus has been calculated. Table 4.5 shows failure probability and bending strength of AYZ samples sintered at 1400°C for 3 hours. From the table it is clear that the powder processing method plays a vital role on the reliability of ceramic materials. The wet milled samples show Weibull modulus values around 15 which is fairly good. But for the dry milled samples, the Weibull modulus values are around 5 which show the poor reliability of this type of samples. Figures 4.6 to 4.11 show the Weibull plots for the wet and dry milled samples.

Tables 4.6 and 4.7 show the various mechanical properties of the Ce-, Y-, and co-doping of these two compounds with zirconia. It is observed that all the mechanical properties change with respect to the powder processing route, fabrication conditions and composition. It is also observed that all the mechanical properties are not simultaneously improved as discussed earlier in the Chapter I.
Table 4.5

Failure probability and bending strength of AYZ samples sintered at 1400°C for 3 hrs.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Bending Strength MPa</th>
<th>Failure Probability (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>339.68</td>
<td>4.76</td>
</tr>
<tr>
<td>2.</td>
<td>342.12</td>
<td>9.52</td>
</tr>
<tr>
<td>3.</td>
<td>346.22</td>
<td>14.28</td>
</tr>
<tr>
<td>4.</td>
<td>347.35</td>
<td>19.05</td>
</tr>
<tr>
<td>5.</td>
<td>348.70</td>
<td>23.81</td>
</tr>
<tr>
<td>6.</td>
<td>354.61</td>
<td>28.57</td>
</tr>
<tr>
<td>7.</td>
<td>356.58</td>
<td>33.33</td>
</tr>
<tr>
<td>8.</td>
<td>360.10</td>
<td>38.01</td>
</tr>
<tr>
<td>9.</td>
<td>362.41</td>
<td>42.86</td>
</tr>
<tr>
<td>10.</td>
<td>365.52</td>
<td>47.62</td>
</tr>
<tr>
<td>11.</td>
<td>368.82</td>
<td>52.38</td>
</tr>
<tr>
<td>12.</td>
<td>374.12</td>
<td>57.14</td>
</tr>
<tr>
<td>13.</td>
<td>377.84</td>
<td>61.90</td>
</tr>
<tr>
<td>14.</td>
<td>382.11</td>
<td>66.67</td>
</tr>
<tr>
<td>15.</td>
<td>387.21</td>
<td>71.43</td>
</tr>
<tr>
<td>16.</td>
<td>391.55</td>
<td>76.19</td>
</tr>
<tr>
<td>17.</td>
<td>396.61</td>
<td>80.95</td>
</tr>
<tr>
<td>18.</td>
<td>402.08</td>
<td>85.71</td>
</tr>
<tr>
<td>19.</td>
<td>407.20</td>
<td>90.48</td>
</tr>
<tr>
<td>20.</td>
<td>411.15</td>
<td>95.24</td>
</tr>
</tbody>
</table>

* Failure probability $P_8 = \frac{i}{N+1}$

Where $i =$ ranking of bending strength in ascending order
$N =$ total number of samples tested
Failure probability (%)

Bending strength (MPa)

Figure 4.6 Weibull plot for the ACZ samples fired at 1400°C for 3 hours
Figure 4.7 Weibull plot for the AYZ samples sintered at 1400°C for 3 hours
Figure 4.8 Weibull plot for the AYCZ samples sintered at 1500°C for 5 hours.
Figure 4.9 Weibull plot for the CZ samples sintered at 1500°C for 3 hours.
Figure 4.10 Weibull plot for the YZ samples sintered at 1500°C for 3 hours.
Figure 4.11 Weibull plot for the YCZ samples sintered at 1500°C for 5 hours.
Table 4.6

Comparision of mechanical properties of Y-, and Ce-Zirconia Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density g/cc</th>
<th>Hardness GPa</th>
<th>$K_{IC}$ MPam$^{1/2}$</th>
<th>$\sigma_f$ MPa</th>
<th>Preparation route</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Ce</td>
<td>6.2</td>
<td>8.7</td>
<td>--</td>
<td>16</td>
<td>Electro refined</td>
<td>Chen &amp; Brook (1989)</td>
</tr>
<tr>
<td>10.8 Ce</td>
<td>6.14</td>
<td>8.8</td>
<td>--</td>
<td>--</td>
<td>Electro refined</td>
<td>Heapworth &amp; Pindar (1987)</td>
</tr>
<tr>
<td>9.1 Ce</td>
<td>6.15</td>
<td>9.8</td>
<td>10*</td>
<td>--</td>
<td>Electro refined</td>
<td>Heapworth &amp; Pindar (1987)</td>
</tr>
<tr>
<td>10 Ce</td>
<td>6.26</td>
<td>--</td>
<td>--</td>
<td>6</td>
<td>Precipitation</td>
<td>Tsukuma (1986)</td>
</tr>
<tr>
<td>10 Ce</td>
<td>6.14</td>
<td>7.64</td>
<td>7.0</td>
<td>6.0</td>
<td>Sol-gel</td>
<td>Present work</td>
</tr>
<tr>
<td>6Y@</td>
<td>6.04</td>
<td>13.70</td>
<td>2.2</td>
<td>--</td>
<td>Tosoh USA</td>
<td>Cutler et al (1992)</td>
</tr>
<tr>
<td>5Y@</td>
<td>--</td>
<td>--</td>
<td>3*</td>
<td>--</td>
<td>Sol-gel</td>
<td>Gokhale et al (1994)</td>
</tr>
<tr>
<td>4y@</td>
<td>--</td>
<td>--</td>
<td>3.5*</td>
<td>--</td>
<td>Sol-gel</td>
<td>Gokhale et al (1994)</td>
</tr>
<tr>
<td>4.5Y@</td>
<td>--</td>
<td>--</td>
<td>6*</td>
<td>--</td>
<td>--</td>
<td>Masaki &amp; Kobayashi (1988)</td>
</tr>
<tr>
<td>5Y</td>
<td>5.92</td>
<td>10.11</td>
<td>4.1</td>
<td>4.8</td>
<td>Sol-gel</td>
<td>Present work</td>
</tr>
</tbody>
</table>

*Indentation method
@HIPed samples
#CIPed followed by sintering
Table 4.7
Comparison of mechanical properties of (Y, Ce)-Zirconia Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fired Temp. °C</th>
<th>Density g/cc</th>
<th>Hardness GPa</th>
<th>$K_{IC}$ MPa*m$^{1/2}$</th>
<th>$\sigma_f$ MPa</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(2.5Y, 4Ce)</td>
<td>1500</td>
<td>6.03</td>
<td>--</td>
<td>--</td>
<td>1000</td>
<td>Hirano (1992)</td>
</tr>
<tr>
<td>(2.5Y, 5.5Ce)</td>
<td>1550</td>
<td>6.00</td>
<td>--</td>
<td>--</td>
<td>860</td>
<td>Hirano (1992)</td>
</tr>
<tr>
<td>(4Y, 4Ce)</td>
<td>1500</td>
<td>6.05</td>
<td>--</td>
<td>7.96*</td>
<td>840</td>
<td>Hirano (1992)</td>
</tr>
<tr>
<td>(4Y, 6Ce)</td>
<td>1400</td>
<td>--</td>
<td>11.00</td>
<td>6.20</td>
<td>-</td>
<td>Boutz et al (1995)</td>
</tr>
<tr>
<td>(4Y, 7Ce)</td>
<td>1500</td>
<td>6.04</td>
<td>--</td>
<td>5.40*</td>
<td>400</td>
<td>Present work</td>
</tr>
<tr>
<td>(4Y, 8Ce)</td>
<td>1400</td>
<td>--</td>
<td>11.00</td>
<td>5.60</td>
<td>-</td>
<td>Boutz et al (1995)</td>
</tr>
<tr>
<td>(1Y, 12Ce)</td>
<td>1500</td>
<td>--</td>
<td>8.7</td>
<td>15</td>
<td>--</td>
<td>Duh et al (1988)</td>
</tr>
<tr>
<td>(2Y, 12Ce)</td>
<td>1500</td>
<td>--</td>
<td>9.2</td>
<td>6</td>
<td>--</td>
<td>Duh et al (1988)</td>
</tr>
</tbody>
</table>

*Urabe et al (1988)
+Notch has been prepared in the green stage itself
4.7 CONCLUSION

Mechanical properties such as hardness, fracture toughness and flexural strength have been evaluated for samples CZ, YZ, YCZ, ACZ, AYZ and AYCZ.

For CZ and ACZ samples, the hardness value varies from 6.5 GPa to 7.64 GPa. The ACZ samples show higher hardness value as 7.64 GPa. The YZ and AYZ samples have the hardness value ranging from 7.7 to 10.98 GPa with the maximum value for AYZ samples. The observed value for the YCZ and AYCZ samples ranges from 9.5 to 10.54 GPa. The hardness studies also show that the yttria containing samples have higher values.

In order to obtain a more reliable fracture toughness value, the notches (SENB and CVNB) are made on the green stage itself and subsequently sintered.

Determination of fracture toughness reveals that the CZ and ACZ samples have higher toughness values than others. The toughness value varies from 6.5 to 7.4 MPam$^{1/2}$. The observed toughness values are almost same for the yttria containing samples. The values vary from 4 to 5 MPam$^{1/2}$ for the yttria containing samples.

Evaluation of flexural strength shows that there are considerable variations in the observed values. The CZ and ACZ samples have average strength of 200 and 262 MPa respectively. The flexural strength values for YZ, YCZ, AYZ and AYCZ samples are 277, 284, 371 and 400 MPa respectively.
Weibull modulus for the dry milled samples is around 5, whereas a value of around 15 has been observed for the wet milled samples. From this it can be concluded that the reliability of the wet milled samples is more than the dry milled samples.

Fracture morphology of the Ce-TZP samples shows the intergranular fracture mode whereas, the other yttria containing samples show the transgranular fracture mode.