CHAPTER-4

EXPERIMENTAL INVESTIGATIONS ON

$(ZrO_2)_{0.8} (Y_2O_3)_{0.2}$ CERAMIC COMPOUND
4.1 INTRODUCTION

Stabilized zirconia (ZrO₂) has been widely used for many years. The ever increasing applications of the oxide in high technology ceramics, particularly in wear parts and as solid electrolytes, has attracted a great deal of attention [1]. Owing to their important applications as high temperature materials, Zirconia ceramics have received considerable attention from the view point of their sintering behaviour and control of the microstructures which develop during the sintering process, so that the resulting materials meet the requirements needed for these applications. In order to produce high performance Zirconia ceramics, solid state sintering has traditionally been adopted as the favoured fabrication route. This route has often required the use of high firing temperature for the achievement of high density in Zirconia materials. Several approaches have proved to be effective in reducing these temperatures. Amongst these approaches, the use of reactive powders such CaO, Y₂O₃ or rare earths oxides has received particular attention [2]. It has been reported that yttria (Y₂O₃) stabilized Zirconia compacts sintered at 1200°C are found to have the highest density [3]. Zirconia-based coatings are commonly used as thermal barrier coatings (TBCs) are increasingly being employed to provide thermal insulation to critical air-cooled mechanical components of gas turbine engines, thereby improving their efficiency [4]. There are three well defined polymorphs in ZnO₂ based ceramic materials namely,
monoclinic, tetragonal and cubic phases [5]. It has been stabilized in cubic phase by the addition of variable amounts of \( R_2O_3 \) (\( R = \) rare earth or yttrium) or CaO. One of the best stabilizers is \( Y_2O_3 \)[6].

The phase diagram of the \( \text{ZrO}_2-Y_2O_3 \) system indicates that the cubic phase exits in the range of composition from 6 to 40 mole % \( Y_2O_3 \) [6]. In the case of \( \text{ZrO}_2-Y_2O_3 \) solid solution the stabilization of cubic phase takes place when the concentration of \( Y_2O_3 \) is not more than 10 mole %[8].

In the present chapter, the polycrystalline ceramic sample of \( (\text{ZrO}_2)_{0.8} (Y_2O_3)_{0.2} \) pure as well as doped with a 1 wt% concentration of transition (Ti, Cu & Mn) elements were synthesized in order to investigate their structural and magnetic feature using X-Ray diffraction (XRD), Scanning electron microscopy (SEM) and Electron paramagnetic resonance (EPR). EPR is hoped to provide information about the valence state of the transition metal ions doped in the ceramic and about the local environment of the doped transition metal ions. The structural information obtained from XRD and Electron microscopy can be correlated with the EPR results together more understanding regarding the micro structural and other properties of the ceramics. The results of these studies will be summarized and discussed in this chapter.

### 4.2 EXPERIMENTAL STUDY

The synthesis of polycrystalline ceramic samples of required stoichiometry in pure as well as doped form has been done using standard high temperature solid state reaction technique. This
technique involves grinding of the constituents together followed by
pelletization and sintering at high temperature. High purity (99.99%) Zr
and Y from Aldrich (USA) in the desired stoichiometry of (ZrO₂)₀.₈
(Y₂O₃)₀.₂ were taken. The transition metal impurities were taken in the
following form for the purpose of doping.

Cu(NO₃)₃H₂O, MnCl₂4H₂O and TiO₂. A fixed concentration (1 wt %)
of the impurity complex was added to the base ceramic. All the
constituents were well mixed together in an agate mortar and pestle
and then palletized in the form of thin cylindrical pellets under the
application of a pressure of 6 ton/cm². The palletized materials were
kept for sintering at a temperature of 1550°C in a glower furnace for
24 hours. Thus formed materials were then characterized through X-ray
diffraction (XRD), scanning electron microscopy (SEM) and electron
paramagnetic resonance (EPR) techniques in order to investigate their
structural and magnetic properties. The sample code and the
composition are given in Table 4-I.

The XRD patterns of all the samples were recorded using a Rich
Seifert Isodebyflex 2002 diffractometer and Cuα radiation with
monochromator. The recording conditions were scan speed (ss) 3°/min,
Time constant Tc= 10 sec., count per minute (CPM) 5K, current/
voltage = 20 MA/30KV. The SEM micrographs were taken using a JEOL
840 SEM. All the micrographs were taken a fixed magnification of x
2500 at 15 KV. EPR measurements were done with the help of an X-
band EPR spectrometer (Varian – E-109) using 100 KHz phase
sensitive detection. The phase composition of the samples have been
evaluated using the XRD studied. The size of grains and morphological
features have been studied with the help of SEM. EPR measurements were carried out to examine the magnetic state of the impurity ion and various changes during and after the synthesis of the samples. The results obtained through the above techniques are presented and discussed here.

4.3 RESULTS AND DISCUSSION

(A) X-ray diffraction:

Fig 4.1(a) shows the x-ray diffraction (XRD) pattern for sample SZYP. It is evident that the XRD pattern consist of three phases namely, monoclinic, tetragonal and cubic. After indexing the observed XRD pattern values are calculated. The observed value of \( d(dobs) \), calculated values (\( d(cal) \)), the miller indices and relative intensities of the peaks are collated in Table 4-II. The values of dobs are calculated using Bragg’s formula:

\[
d_{\text{obs}} = \frac{\lambda}{2 \sin \theta}
\]  

where \( \lambda \) is the wavelength of Cu-K\( \alpha \), \( \theta \) is the diffraction angle and \( d_{\text{obs}} \) is the interplaner distance.

The values of \( d_{\text{cal}} \) have been calculated using the following expressions and lattice parameters from literature [7,8]:

For cubic \( \frac{1}{d^2_{\text{cal}}} = \frac{(h^2+k^2+l^2)}{a^2} \)  (4.3.2)

For tetragonal \( \frac{1}{d^2_{\text{cal}}} = \frac{(h^2+k^2)}{a^2 + l^2 / c^2} \)  (4.3.3)

For monoclinic

\[
\frac{1}{d^2_{\text{cal}}} = \left[ \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2 - 2hl \cos(\beta)/ac} \right] / \sin^2 \beta
\]  (4.3.4)

The phase composition for the samples has been evaluated using
intensity variation semiempirical method [9,10]. In order to make quantitative analysis of the monoclinic, tetragonal and cubic phases existing in the samples, we have used the following expressions:

\[ I_m = \frac{[I_m(1\overline{1}1)+I_m(111)] \times 100}{[I_m(1\overline{1}1)+I_m(111) + I_c(111)]} \] (4.3.5)

\[ I_t = \frac{(I-I_m)[I_t(400)+I_t(004)] \times 100}{[I_t(400)+I_t(004)+I_c(400)]} \] (4.3.6)

And \(I_c + I_m + I_t = 100\)

Where \(I_m\), \(I_t\) and \(I_c\) are the percentages of Monoclinic, Tetragonal and Cubic phases respectively. We have assumed that the intensities of various peaks of respective phases represent the amount of the particular phases, for example intensity of reflection (111) represents the amount of monoclinic phase.

Fig 4.1 (b to d) depict the XRD patterns for samples SZYTi, SZYMn and SZYCu. All samples exhibit essentially the same kind of patterns. The percentage of phase composition of the samples has been estimated and the values obtained are given in Table 4-III.

From the above crystallographic data, we can say that all four samples exhibit monoclinic phases as the dominant phase. It is also worth mentioning that in earlier studies ZrO₂ doped with 12 mol % of \(Y_2O_3\) were found to contain almost monoclinic phase [5].

(B) Scanning Electron Microscopy Studies:

The SEM micrographs for all the samples are shown on Fig 4.2 (a-d). It is evident from the micrographs that all samples comprise two major kinds of phases. One of them being brighter (white), while the other is darker (black). At the time of preparation of these samples for
SEM studies, we have observed an interesting fact that during the sputtering of Ag metal upon the sample, there was illumination of light. We can attribute this phenomenon to luminescence of materials. All the samples seem to have the nearly uniform microstructure. The average grain size varies from sample to sample. Generally sintering temperature, duration preparation methods, particle size of unsintered mixture etc., are the parameters which affect the microstructure of the final product. It should be stressed here that we have subjected a fixed heat treatment for sintering to all the samples. Therefore, the variation in average grain size may be attributed to the effect of various dopants.

It may also be noted from these micrographs that all samples display an overall increase in grain-size as compared to the pure sample SZYP. This increase probably results due to the presence of impurity ions which favours the particles assemblage of doped samples. The grain size estimates obtained from the SEM pictures indicate two ranges of particle-size; larger grains (> 5 µm) and smaller grains (< 1 µm).

(c) Electron Paramagnetic Resonance Studies

(i) Pure sample SZYP:

The EPR spectrum of the powdered (finely crushed) undoped sample SZYP comprise a narrow resonance line near $g = 2$ superimposed on a broad EPR signal spectrum for pure sample (SZYP). Fig 4.3 shows EPR spectrum of SZYP at RT. As mentioned earlier we have used 99.99 % pure ZrO$_2$ for synthesizing the SZYP samples, therefore the presence of any extrinsic paramagnetic impurity
is not expected. However the sample indicates the presence of some
paramagnetic centers in the synthesized material SZYP. It is not
possible to identify the exact nature and cause of these centers. The
narrow signal is situated at $g_{\text{eff}} = 1.975 \pm 0.005$ and the width of this
signal $\Delta H$ is $\equiv 25 \pm 3G$. The width of the broad signal is $\equiv 290G$ and is
situated around $g_{\text{eff}} \equiv 2.05$. These paramagnetic centers may be artefact
of synthesis process since these signal are present in all the samples
prepared for the present study. The interesting aspect of these signals
is that their widths and positions remain essentially temperature
independent between RT and LNT[11]. The narrow signal is marked by
p and its position is denoted by $g_p$ is given in table 4-IV where the
parameters obtained from EPR study are collated. As revealed by X-ray
the SZYP sample comprise mainly monoclinic and tetragonal phases.
The two signals may result from these phases present in the
synthesized sample.

(ii) Titanium Doped Sample SZYTi:

The EPR spectrum of Titanium doped sample (Fig. 4.4)comprises a
large number of narrow lines in addition to Titanium has the electronic
structure [A] 3d$^2$4S$^2$. The two signals Divalent titanium complexes are
very unstable. However trivalent titanium observed in SZYTi, with
electronic configuration [A] 3d forms octahedral paramagnetic
complexes which are stable. Titanium has several isotopes viz. $^{44}\text{Ti}$,
$^{47}\text{Ti}$, $^{48}\text{Ti}$, $^{49}\text{Ti}$ and $^{50}\text{Ti}$. Hyperfine splitting may arise only due to $^{47}\text{Ti}$ and
$^{49}\text{Ti}$ as they have none zero nuclear spins I of 5/2 and 7/2 respectively
and for the even isotopes the nuclear spin is zero. In octahedral and
tetrahedral environments $\text{Ti}^{3+}$ has an orbital singlet as its ground state and there are low lying excited state. EPR spectra can be observed at RT and LNT and are appropriate to $S=1$ like $\text{Ni}^{2+}$ [12-14].

The $g$ factor is expected to be less than $g_e (= 2.0023)$ EPR is appropriate to $S = 1/2$. The observed EPR spectrum in the present case are not appropriate to any of the above two paramagnetic states of Titanium. The observed increase in line width of the broad spectrum as compared to SZYP indicates that Titanium ion is having some exchange interaction with the paramagnetic center responsible for the broad EPR signal. The presence of a large number of narrow lines on the broad signal may be attributed to superhyperfine interaction between the paramagnetic center and surrounding ligands which probably involves Titanium nuclear spins. The structure is too complex to be analyzed meaningfully.

(iii) Manganese Doped Sample SZYMn:

The EPR spectrum of manganese doped sample is shown in Fig 4.5. In addition to the two signals observed for the undoped sample SZYP two more signals are observed. The positions are described by the effective $g$-values ($g_b \approx 2.1$ and $g_c \approx 2.0$ and the line widths are $\Delta H_b \approx 16$ G and $\Delta H_c \approx 25$ G). Divalent manganese $\text{Mn}^{2+}$ has $d^5$ electronic state and the free ion ground state is $^6S_{5/2}$. The 6 fold spin degeneracy is lifted by spin-orbit coupling giving rise to three Kramers doublets. In general there are $(2S + 1) = 5$ allowed EPR transitions corresponding to $M= \pm 1$. Due to the nuclear spin $I = 5/2$ each fine structure transition shows a characteristic hyperfine splitting into six components.
corresponding to \( m=0 \). Therefore, a thirty line spectrum is expected for \( \text{Mn}^{2+} \) in a crystal \([12-18]\). The observed structure less narrow line at \( g \approx 2.2 \) could be attributed to an exchange narrowed EPR signal of \( \text{Mn}^{2+} \) impurities. Such single line EPR signal of \( \text{Mn}^{2+} \) provides an indication that manganese forms a concentrated phase in the host matrix. This may result due to aggregates of manganese(II) complex formed in the host matrix similar to Suzuki phase in alkali halides \([20]\). The EPR parameters of the observed EPR signals corresponding to fig 4.5 for SZYMn are collated in Table 4-IV. The origin of the second signal at \( g \approx 2.1 \) is not known. It is interesting to compare these results with those reported by Stempki et al \([21]\) for manganese doped signal crystals of \((\text{ZrO}_2)_{0.8-}(\text{Y}_2\text{O}_3)_{0.2}\). They have observed a six line spectrum at \( g= 2 \) with hyperfine parameter \( A \approx 83\text{G} \) and attributed it to \( \text{Mn}^{2+} \) ion substituting either \( \text{Zr}^{4+} \) or \( \text{Y}^{3+} \) ions at lattice sites. It was suggested that a trigonal distortion occurs probably due to charge compensation requirements\([22]\). Our results indicate that in SZYMn sample a phase separation of manganese complex occurs. However, this could be confirmed using X-ray and SEM studies because of inadequate resolution and low impurities concentration.

**(iv) Copper Doped Sample SZYCu:**

Powder EPR spectrum of copper doped sample is shown in fig 4.6. As explained in earlier chapter \( \text{Cu}^{2+} \) with 3\(d^9 \) configuration may be regarded as a single hole in the filled 3\(d^{10} \) configuration\([23]\). Its EPR spectrum would be similar to \( d^4 \) configuration. Since the two naturally occurring isotopes of copper (\( ^{63}\text{Cu} \) and \( ^{65}\text{Cu} \)) have nuclear spins \( I= 3/2, \)
the EPR spectra are explained by the following spin Hamiltonian with $S = \frac{1}{2}$ and $I = 3/2$: [12- 15].

$$\mathcal{H} = \beta S g H + I A S$$ \hfill (4.3.7)

In the powdered sample one observes characteristic peaks corresponding to parallel ( $||$ i.e $\theta = 0^0$ ) and perpendicular ( $\perp$ i.e $\theta = 90^0$ ) orientations in axial symmetry [18,19]. The $||$ and $\perp$ components are identified in the EPR spectrum of copper doped sample SZYCu shown in Fig. 4.6. The values of $A_||$ and $A_\perp$ are given in Table 4 IV. Hence the unpaired electron resides in $d_{x^2-y^2}$ ground state orbital and Cu$^{2+}$ ion experiences a tetragonally distorted octahedral crystal field around it [18] in host under study.

### 4.4 Conclusion

The results of EPR, SEM and XRD studies of $(ZrO_2)_{0.8}(Y_2O_3)_{0.2}$ samples synthesized by solid state reaction route show that the favourable phases are monoclinic and tetragonal. Small amount of doped impurities of transition metal ions are not found to change the composition of the system noticeably. However, EPR studies reveal that Copper enter the host lattice in paramagnetic valence states. The copper ion is in Cu$^{2+}$ state and its ground state is $d_{x^2-y^2}$. 
Table 4-I.
Sample codes and doped impurity

<table>
<thead>
<tr>
<th>S.NO</th>
<th>Samples</th>
<th>Doped impurity</th>
<th>Stoichiometry of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>SZYP</td>
<td>P</td>
<td>(ZrO$<em>2$)$</em>{0.8}$(Y$_2$O$<em>3$)$</em>{0.2}$</td>
</tr>
<tr>
<td>2.</td>
<td>SZYTi</td>
<td>TiO$_2$</td>
<td>(ZrO$<em>2$)$</em>{0.8}$(Y$_2$O$<em>3$)$</em>{0.2}$</td>
</tr>
<tr>
<td>3.</td>
<td>SZYMn</td>
<td>MnCl$_2$</td>
<td>(ZrO$<em>2$)$</em>{0.8}$(Y$_2$O$<em>3$)$</em>{0.2}$</td>
</tr>
<tr>
<td>4.</td>
<td>SZYCu</td>
<td>Cu(NO$_3$)$_2$</td>
<td>(ZrO$<em>2$)$</em>{0.8}$(Y$_2$O$<em>3$)$</em>{0.2}$</td>
</tr>
</tbody>
</table>

* The concentration of each dopant is 1 wt % of (ZrO$_2$)$_{0.8}$(Y$_2$O$_3$)$_{0.2}$ and P stand for pure
### Table 4-II.

**Crystallographic Data**

**Estimated from XRD Studies for SZYP Sample.**  
(M=Monoclinic, T=Tetragonal and C=Cubic)

<table>
<thead>
<tr>
<th>hkl</th>
<th>Phases</th>
<th>(d_{obs}/\AA^0)</th>
<th>(d_{cal}/\AA^0)</th>
<th>((d_{obs}-d_{cal})/\AA^0)</th>
<th>((I/I_0)_{obs})%</th>
</tr>
</thead>
<tbody>
<tr>
<td>[110],[011], [111]</td>
<td>M</td>
<td>3.60</td>
<td>3.64</td>
<td>0.04</td>
<td>24</td>
</tr>
<tr>
<td>[111]</td>
<td>M</td>
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<td>77</td>
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<td>[111]</td>
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<td>100</td>
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<tr>
<td>[111]</td>
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<td>2.84</td>
<td>0.04</td>
<td>76</td>
</tr>
<tr>
<td>[200],[002]</td>
<td>M,C</td>
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<tr>
<td>[210]</td>
<td>M</td>
<td>2.30</td>
<td>2.28</td>
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<td>8</td>
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<tr>
<td>[102]</td>
<td>M</td>
<td>2.17</td>
<td>2.18</td>
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<tr>
<td>[112]</td>
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<td>0.04</td>
<td>10</td>
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<tr>
<td>[112]</td>
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<td>[113],[311],</td>
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<td>1.55</td>
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<td>[311],[131]</td>
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<td>C,M</td>
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<td>[132]</td>
<td>T</td>
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<td>[104]</td>
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<tr>
<td>[400],[004]</td>
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<tr>
<td>[400]</td>
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<td>-</td>
<td>1.22</td>
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<td>T</td>
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<td>1.10</td>
<td>0.00</td>
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<td>[004]</td>
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<td>1.09</td>
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</tbody>
</table>
Table 4-III.

Shows the relative phase composition

<table>
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<tr>
<th>S.No</th>
<th>Samples Code</th>
<th>M</th>
<th>T</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SZYP</td>
<td>61</td>
<td>33</td>
<td>6</td>
</tr>
<tr>
<td>2</td>
<td>SZYTi</td>
<td>58</td>
<td>33</td>
<td>9</td>
</tr>
<tr>
<td>3</td>
<td>SZYMn</td>
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<tr>
<td>4</td>
<td>SZYCu</td>
<td>62</td>
<td>32</td>
<td>6</td>
</tr>
</tbody>
</table>

M= Monoclinic, T= Tetragonal and C= Cubic

Table 4-IV.

Parameter Derived from EPR Studies

<table>
<thead>
<tr>
<th>Samples Code</th>
<th>G Values</th>
<th>Hyper fine parameters A (Gauss)</th>
<th>Line width $\Delta$ H (Gauss)</th>
</tr>
</thead>
</table>
| SZYP         | $g_p = 1.975 \pm 0.005$  
$g_a = 2.05 \pm 0.05$ | ---                             | $\Delta H_p = 23 \pm 3$,  
$\Delta H_a = 290 \pm 20$ |
| SZYTi        | $g_p = 1.975 \pm 0.005$  
$g_a = 3.7536 \pm 0.05$ | ---                             | $\Delta H_p = 25 \pm 3$,  
$\Delta H_a = 1687 \pm 50$ |
| SZYMn        | $g_p = 1.975 \pm 0.005$  
$g_a = 2.10 \pm 0.05$  
$g_c = 2.001 \pm 0.005$ | ----                           | $\Delta H_p = 25 \pm 3$,  
$\Delta H_a = 16 \pm 4$,  
$\Delta H_c = 25 \pm 2$ |
| SZYCu        | $g_p = 1.975 \pm 0.005$ | $A_{||} = 56, A_{\perp} = 24$ | $\Delta H = 22 \pm 3$         |
Fig. 4.1 (c & d) X-ray diffraction patterns of samples SZYMn & SZYCu
4.2 (a and b) SEM MICROGRAPHS OF SAMPLE SZYP AND SZYTI
Fig. - 4.2 (c and d) SEM MICROGRAPHS OF SAMPLE SZYMn AND SZYCu
Fig. 4.3 EPR spectrum of sample SZYP at room temperature
Fig. 4.4 EPR Spectrum of sample SZYTi
REFERENCES


