IN THE NAME OF GOD

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PREPARATION AND OPTIMIZATION PROPERTIES OF OXYGEN SENSOR

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THESIS

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TO MY MOTHER

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ABSTRACT

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MOJTABA GHATEE

In the present research cubic/tetragonal zirconia composite solid electrolyte was prepared by two different processing techniques including solid oxide mixing of 3 mol% yttria stabilized zirconia (3YSZ) and 8 mol% yttira stabilized zirconia (8YSZ), and also net shape forming. Net shape forming was performed by impregnation of 3YSZ and 8YSZ with yttria/scandia and zirconia solutions respectively. The microstructure and phase assemblage was investigated by SEM and XRD. The electrical conductivity of samples was measured by impedance spectroscopy at different temperatures. Hardness and fracture toughness of samples were investigated by Vickers hardness indentation method and the mechanical strength was measured by ring on ring test methods. It was shown that increasing tetragonal phase content of samples decreased the electrical conductivity of composite electrolytes at high temperatures while it was vice versa at low temperatures. In addition increasing the tetragonal phase content of sample improved mechanical properties of composites. In general solid oxide mixing was a simple preparation technique while better combination of electrical and mechanical properties along with core/shell structure obtained by net shape forming technique. It was found that electrolytes with conductivity of 0.08 S/cm at 900 °C and mechanical strength and fracture toughness of respectively 375 MPa and 4.1 MPa $m^{1/2}$ can be obtained by addition of 35 wt.% 3YSZ to 8YSZ using solid oxide mixing. However the best combination of mechanical and electrical was obtained by impregnation of 3YSZ with scandia solution by which electrolytes with conductivity of 0.12 S/cm at 900 °C and mechanical strength and fracture toughness of respectively 480 MPa and 4.3MPa $m^{1/2}$ were prepared. It was also found that composite electrolytes had lower activation energy of electrical conductivity along with higher electrical conductivity at low temperatures (T<550°C). In all composite samples the grain boundary contribution to total conductivity was lower with respect to pure constituents which means that composite effect, which is normally occur in conductor/insulator composites, observed in composites of two ionic conductors.

TABLE OF CONTENT

Content Page

Content Page

LIST OF TABLES

LIST OF FIGURES

Content Page

Content Page

Content Page

1. Introduction

1.1. Preface

Zircon has been known as a gem from ancient times. The name of the metal, zirconium, comes from the Persian word Zargon (golden in colour) which in turn comes from the two Persian words Zar (Gold) and Gun (Like) (Picconi 1999). Zirconia, the metal dioxide (ZrO2), was identified as such in 1789 by the German chemist Martin Heinrich Klaproth in the reaction product obtained after heating some gems, and was used for a long time blended with rare earth oxides as pigment for ceramics (Picconi 1999). Zirconia is a well-known polymorph that occurs in three forms: monoclinic (M), cubic (C) and tetragonal (T). (Picconi 1999).

Pure zirconia is monoclinic at room temperature. This phase is stable up to 1170°C. Above this temperature it transforms into tetragonal and then into cubic phase at 2370°C. During cooling, the tetragonal to monoclinic transformation takes place in a temperature range of about 100°C below1070°C (Xue 2005).

$$\mathrm{m\text{-}ZrO_2} \underset{950^\circ\mathrm{C}}{\overset{1170^\circ\mathrm{C}}{\rightleftharpoons}} \mathrm{t\text{-}ZrO_2} \overset{2370^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{c\text{-}ZrO_2} \overset{2680^\circ\mathrm{C}}{\rightleftharpoons} \mathrm{liquid}$$

Figure 1 shows the unit cell of there polymorph of zirconia and Table 1 and Table 2 summarized crystallographic characteristic including space group lattice parameter and theoretical density of these polymorphs in yttria-zirconia and scandia-zirconia systems respectively (Hanink 2002). It should be noted the lattice parameters depends on type of dopant used and here the required values which is referred through this work, is presented.

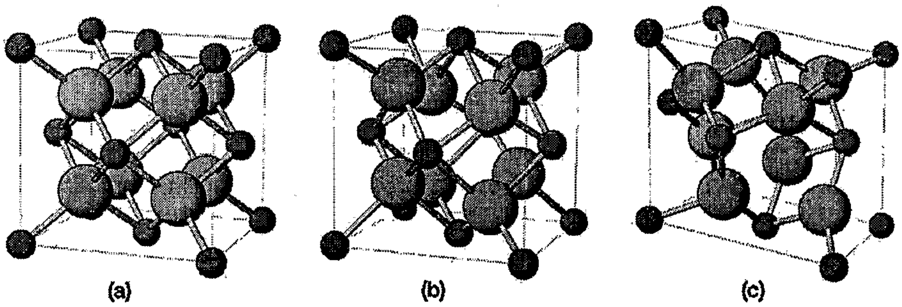

(a) (b) (c)

Figure 1: Unit cell of zirconia polymorph monoclinic (a), tetragonal (b) and cubic (c) (Hannink 2000).

Table 1: Crystallographic characteristics of various zirconia polymorphs in ZrO2-Y2O3 system (Hannink 2002).

Crystal structure	Space group			Unit cell dimension (?)			
		a	b	c	α	β	γ
*Monoclinic	P121/C1	5.14422	5.20969	5.31120	90	99.290	90
Tetragonal	P42/NMC	3.6067	3.6067	5.1802	90	90	90
Cubic	FM3M	5.14728	5.14728	5.14728	90	90	90

*Pure ZrO2

Table 2: Crystallographic characteristics of various zirconia polymorphs in ZrO2-Sc2O3 system (Ciacchi 1991).

Crystal structure	Space group	Unit cell dimension (?)					
		a	b	c	α	β	γ
Monoclinic	P121/C1	5.14422	5.20969	5.31120	90	99.290	90
Tetragonal	P42/NMC	3.5965	3.5965	5.1608	90	90	90
cubic	FM3M	5.091	5.091	5.091	90	90	90

*Pure ZrO2

The monoclinic phase, which is the most stable phase under normal atmospheric pressure at room temperature, has limited practical applications since its formation during cooling from the high temperature tetragonal phase is associated with volume expansion (~5 vol.-%), which results in crumbling of the ceramic components (Evans 1990). However, this tetragonal-to-monoclinic transformation has a great technological importance for mechanical applications since it is the basis for the transformation toughening of ceramic components which will be discussed later (Kelly 2006). ZrO2 has shown excellent performance as extrusion dies for non-ferrous metals and as tool bits and thread guides (Schukla 2005). Various other interesting properties of ZrO2 have lead to its different industrial applications. ZrO2 blades are widely used in cutting tools to cut Kevlar, magnetic tapes, cigarette filters because of their reduced wear and erosion characteristics (Tu 1997). As a result of its very high refractive index close to that of diamond (n = 2.42), ZrO2 has been produced extensively to manufacture synthetic grade jewels and used in ceramic glazes as an opacifier (Subbarao 1981). Moreover, ZrO2 has higher thermal stability and acid-base resistance properties. It is also stable under a reducing atmosphere and photo irradiation (Picconi 1999). These properties make ZrO2 the most suitable candidate as a refractory material and as catalyst/catalyst support for hydrogenation and isomerisation reactions compared with other ceramic oxides (TiO2, SiO2 and Al2O3) (Subbarao 1981). Moreover, owing to their high oxygen ionic conductivity of cubic and tetragonal phases, these high temperature phases of ZrO2 are useful as solid electrolytes in oxygen sensors (Zhuiykov 2008, Garzon 2004, Fergus 2007, Riegel 2002, Ivers-Tiffe´e 2001, Soimov 2000, Maskell 2000, Rodrigues 2000, Nafe 2000) and solid oxide fuel cells (Collongues 1979, Appleby 1988, R. Collongues 1979, Minh 1993), operating at lower temperatures. As a result of their high strength, high fracture toughness, high hardness, and high thermal shock resistance, the cubic or tetragonal ZrO2 is used as a port liner for combustion engines and wire drawing dies (Subbarao 1981). The low thermal conductivity together with relatively low coefficient of thermal expansion allows the use of high temperature polymorphs of ZrO2 (tetragonal and cubic) in thermal barrier coating (TBC) applications (Picconi 1999). Good chemical and dimensional stability, mechanical strength, toughness, coupled with Young's modulus in the same order of magnitude as stainless steel alloys are the origin of the interest in using ZrO2 as a ceramic biomaterial. Currently, zirconia is used to manufacture ball heads for total hip replacement. More than 300000 ball heads made of tetragonal zirconia, has been implanted, and only two failures were reported up to now (Picconi 1999).

The addition of 'stabilizing' oxides, like CaO, MgO, CeO2, Y2O3, to pure zirconia allows stabilizing high temperature tetragonal and cubic phases at low temperatures (Picconi 1999). It should be noted that various kind of dopants can be used as stabilizer including N2, oxide of various elements (Ce, Y, Mg, Sc, La, Nb, Yb, Ca...). Figure 2 and Figure 3 show phase diagrams of ZrO2- Y2O3 and ZrO2-Sc2O3 which are used in the most technologically important fields like oxygen sensors and fuel cells. According to the type and amount of dopant various combinations of phases can be prepared. As can be seen various combination of phases can be stabilized.

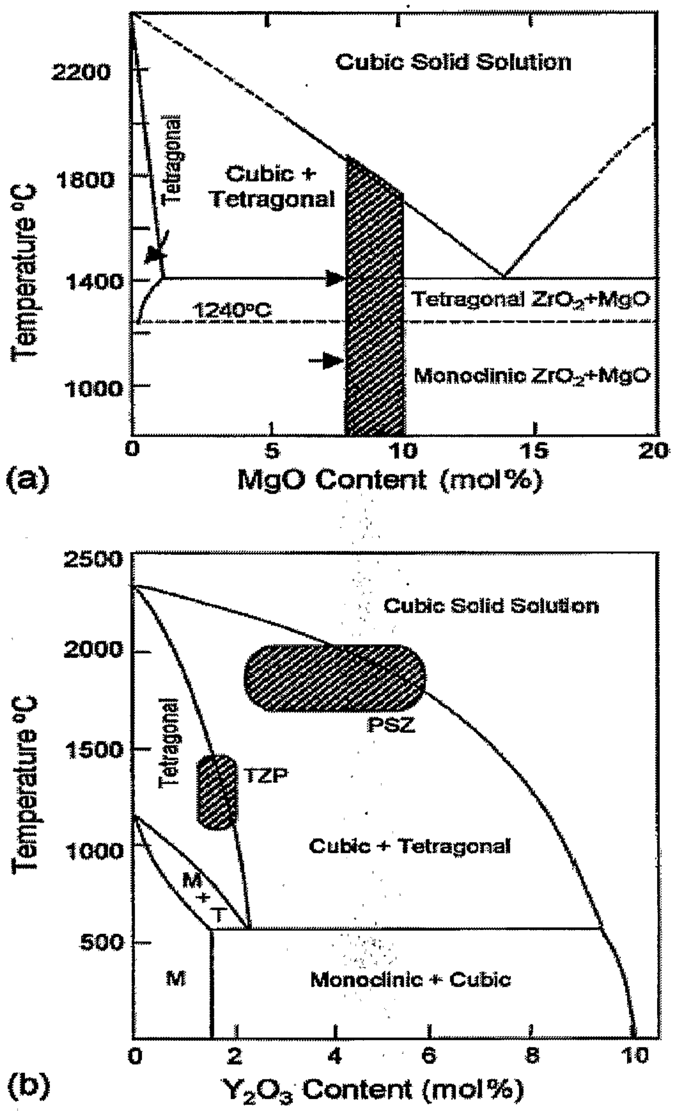


Figure 2: ZrO2-MgO (a) and ZrO2 - Y2O3 (b) phase diagram (Hannink 2000).

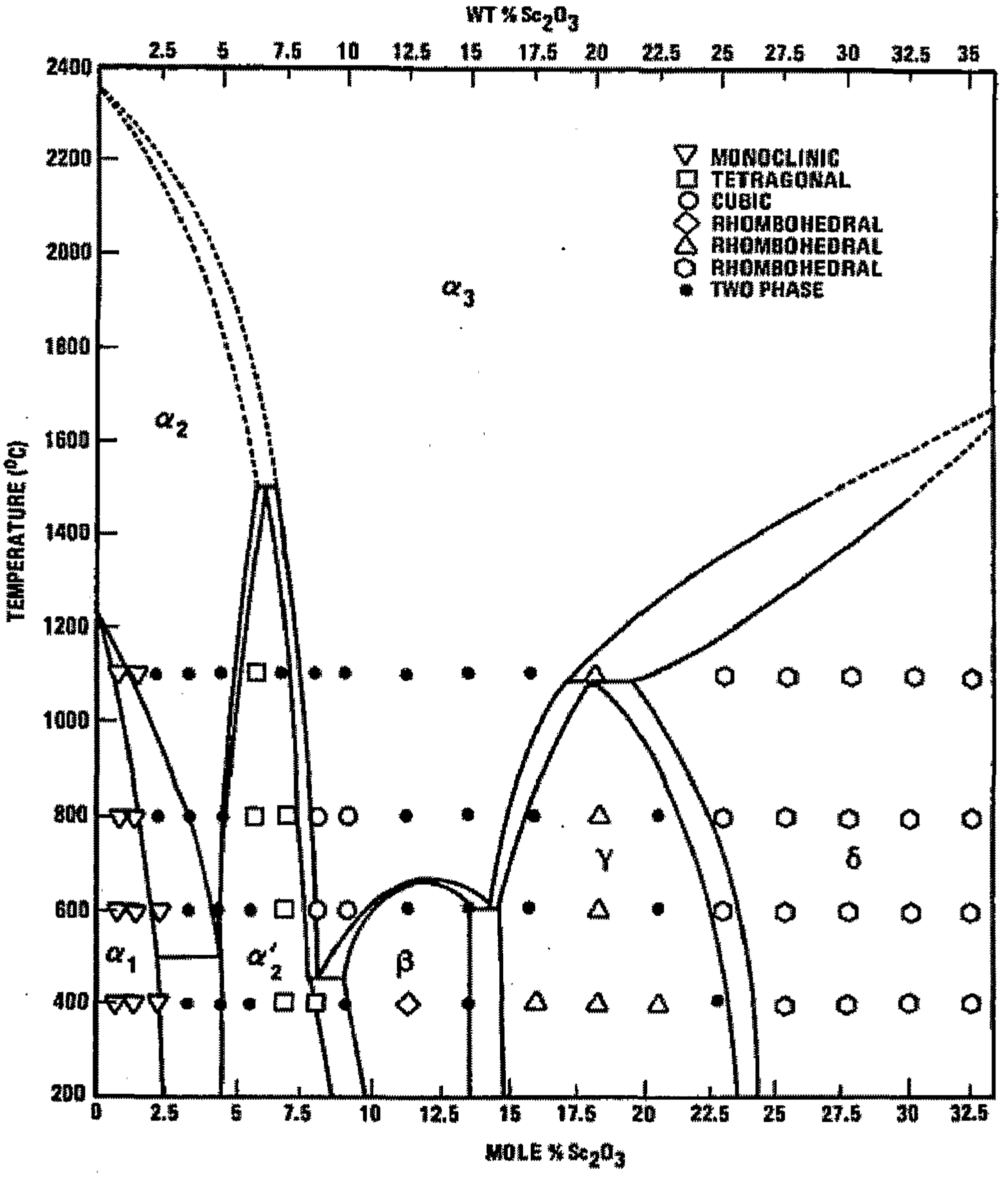
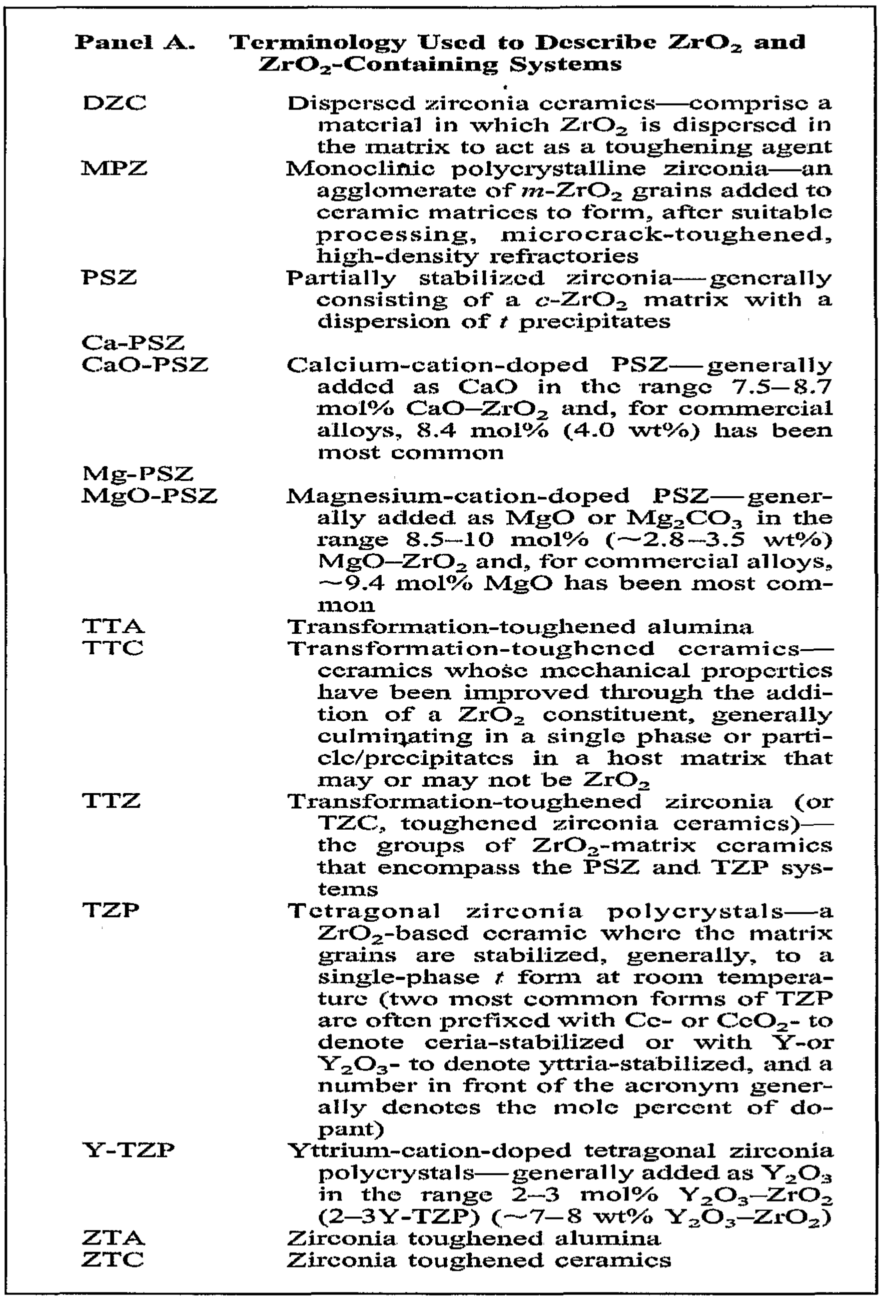


Figure 3: ZrO2 -Sc2O3 phase diagram (Ruh 1977).

Table 3 presents nomenclature of various zirconia and zirconia containing ceramics. Some of these grades which are relevant to this research will be explained briefly through this chapter.

Table 3: Terminology used describe zirconia and zirconia containing ceramics (Hannink 2002).



Panel A.	**Terminology Used to Describe ZrO_2 and ZrO_2-Containing Systems**
DZC	Dispersed zirconia ceramics—comprise a material in which ZrO_2 is dispersed in the matrix to act as a toughening agent
MPZ	Monoclinic polycrystalline zirconia—an agglomerate of m-ZrO_2 grains added to ceramic matrices to form, after suitable processing, microcrack-toughened, high-density refractories
PSZ	Partially stabilized zirconia—generally consisting of a c-ZrO_2 matrix with a dispersion of t precipitates
Ca-PSZ CaO-PSZ	Calcium-cation-doped PSZ—generally added as CaO in the range 7.5–8.7 mol% CaO–ZrO_2 and, for commercial alloys, 8.4 mol% (4.0 wt%) has been most common
Mg-PSZ MgO-PSZ	Magnesium-cation-doped PSZ—generally added as MgO or Mg_2CO_3 in the range 8.5–10 mol% (~2.8–3.5 wt%) MgO–ZrO_2 and, for commercial alloys, ~9.4 mol% MgO has been most common
TTA	Transformation-toughened alumina
TTC	Transformation-toughened ceramics—ceramics whose mechanical properties have been improved through the addition of a ZrO_2 constituent, generally culminating in a single phase or particle/precipitates in a host matrix that may or may not be ZrO_2
TTZ	Transformation-toughened zirconia (or TZC, toughened zirconia ceramics)—the groups of ZrO_2-matrix ceramics that encompass the PSZ and TZP systems
TZP	Tetragonal zirconia polycrystals—a ZrO_2-based ceramic where the matrix grains are stabilized, generally, to a single-phase t form at room temperature (two most common forms of TZP are often prefixed with Ce- or CeO_2- to denote ceria-stabilized or with Y-or Y_2O_3- to denote yttria-stabilized, and a number in front of the acronym generally denotes the mole percent of dopant)
Y-TZP	Yttrium-cation-doped tetragonal zirconia polycrystals—generally added as Y_2O_3 in the range 2–3 mol% Y_2O_3–ZrO_2 (2–3Y-TZP) (~7–8 wt% Y_2O_3–ZrO_2)
ZTA	Zirconia toughened alumina
ZTC	Zirconia toughened ceramics