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Impurities Effect on the Charge Mobility of Yttria-Stabilized Zirconia

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The present study is concerned with the preparation of yttria-stabilized zirconia (YSZ) having high charge mobility. Herein, we studied the doping of zirconia with different concentrations of Y_2O_3. The samples were prepared by a solid state reaction at 800, 1000, and 1200°C for 2 hours. The morphology of the pellets was characterized by scanning electron microscope (SEM). Crystallinity and phase change were studied by X-ray diffraction (XRD). The electrical conductivity of the sintered pellets was measured and demonstrated that the conductivity increase as yttria content increase. We have also found that the conductivity decreased with increasing the level of the impurities in the natural ore.

Keywords: Yttria-stabilized Zirconia; clusters; composite materials; solid state reactions; crystal structures.

1. INTRODUCTION

Zirconia is one of the most common functional ceramics. Pure zirconia exhibits three polymorphic solid state phases as a function of temperature [1]. The monoclinic phase is stable at temperatures below 1170°C. The tetragonal phase is stable between 1170 and 2370°C. The cubic phase is stable at temperature comprised between 2370°C and the boiling point (approximately 2680°C) [2]. However, zirconia suffers from phase changes upon heating associated with the change of monoclinic to tetragonal phase. Doping zirconia with elements such as Y, Ca, Mg stabilizes the tetragonal phase and prevents the volume change associated with the formation of monoclinic phase [3, 4, 5]. Of particular interest, doping zirconia with yttria increases the oxygen ions conductivity which of interest for applications such as oxygen ion sensors and solid oxide fuel cell [6, 7, 8]. The ionic conductivity and oxygen diffusion in yttria –doped zirconia is connected with the presence of vacancies in the oxygen positions in the lattice, which are formed as charge compensating defects when doping zirconia with lower valent cations [9, 10]. The conductivity increases with increasing dopant content, because of increasing concentration of vacancies – until it reaches a maximum (about 10 mol.% Y_2O_3), followed by a decrease at higher concentrations of dopants [11]. The long-range migration of these dissociated vacancies can be studied by applying oxygen tracer diffusion and electrical conductivity experiments [12]. Although the conductivity and oxygen diffusion of YSZ is heavily studied in the literature, the effect of the impurities that might exist in the natural ore is hardly considered. Herein, we demonstrate the relation between the level of the impurities in the natural zirconia ores and the conductivity of YSZ. We found that the conductivity decreases significantly with increasing the impurity level suggesting that the YSZ could be produced from impure row materials with lower charge mobility properties.

2. EXPERIMENTAL

2.1. Preparation of YSZ using analytical grade Y_2O_3 & ZrO_2:

Pure YSZ powder was first prepared by mixing analytical grad ZrO_2 with different concentrations of Y_2O_3 namely 6, 8, 10, 15 and 20 wt. %. A temporary binder (1.5% of paraffin wax) was introduced into the powder, and the samples were cold pressed using a load of 16 ton into cylindrical pellets of about 23mm diameter and 7mm thickness. The pellets were subsequently sintered in air at 800, 1000, and 1200^{o}C for 2 hours. Resistance of the sintered pellets was measured by OMEGA Cl 8400 Micro-Ohmmeter at room temperature and the electric conductivity was calculated. The phase identification was performed by X-ray diffraction (XRD). The scanning electron microscope (SEM) was used to study the surface morphology and microstructure of the obtained YSZ pellets.

2.2. Preparation of YSZ using zirconia produced from natural zircon:

Zirconia is commercially produced from the most abundant zirconium bearing mineral which is the orthosilicate ($ZrSiO_4$) known as zircon. The first step is to break the strong bond between the silica and zirconia via reaction with molten salts, as describe elsewhere [13-15]. Typically, about 180 g of zircon heated with 90 g of sodium hydroxide at 600 °C for 3 hours. The sample was allowed to cool down in the furnace and then leached in hot water in order to remove the water soluble sodium silicate. The remaining sodium zirconate, which has very limited solubility in water, was then removed by filtration. Zirconium was then subjected to a quick purification step by converting it to oxychloride via reaction with hot 1M HCl solution. Next, the over saturated solution was allowed to crystalline into pure $ZrOCl_2$ by leaving the solution stagnant for 3 days. The pure crystals was then filtered out from the solution then redissolved in hot water. Zirconium hydroxide powder was then deposited at the bottom of the crucible by adding sodium hydroxide solution. Finally, the precipitate was separated from the main liquor by filtration then calcined at 1200°C for 2 hours to pure ZrO_2 [13-15]. Zirconia was then subjected to XRD, XRF, and elemental chemical analysis to determine the phase present and the level of impurities respectively. YSZ powder was then prepared by mixing analytical grade yttria with the obtained commercial zirconia with the optimum condition of 20 wt. % Y_2O_3 and sintering at 1000°C for 2 hours. The powder was then pressed and sintered and the electric conductivity was measured.

3. RESULTS AND DISCUSSION

3.1. YSZ prepared using analytical grade Y_2O_3 & ZrO_2:

3.1.1. Phase identification of YSZ by XRD:

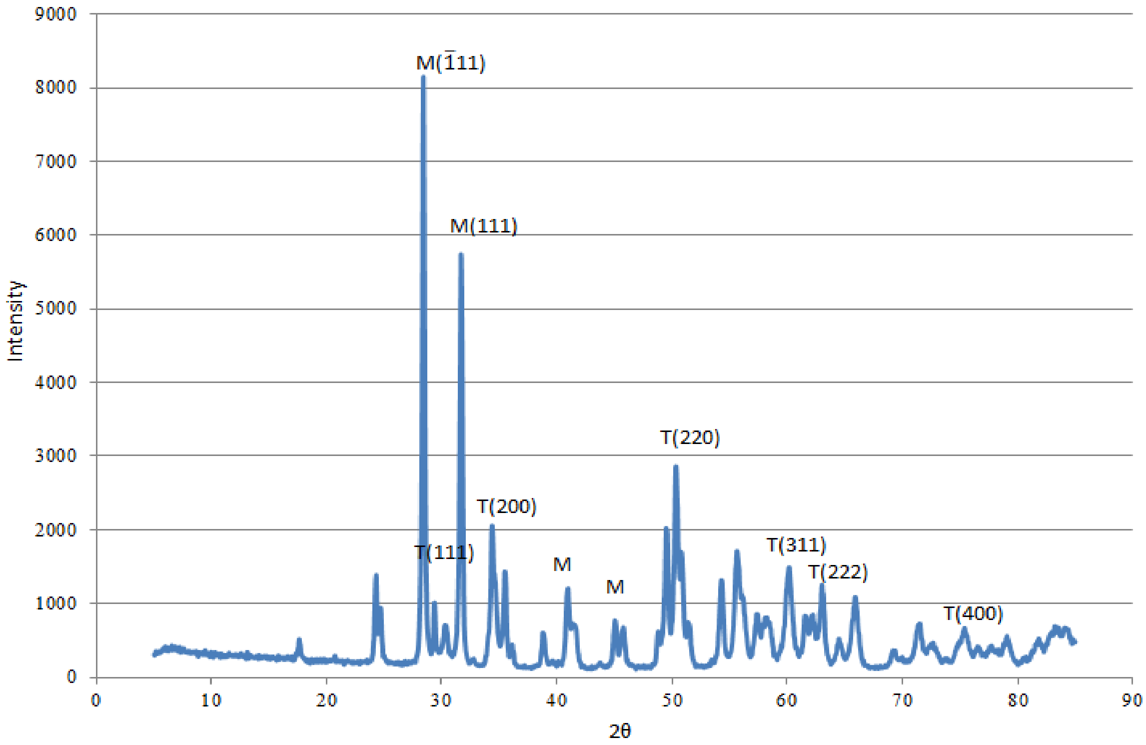

Figure 1. XRD pattern of YSZ sintered at 1200°C (Y_2O_3 content: 6 wt. %)

X-ray diffraction analysis was carried out to determine the crystal structure and phase identification of the powder. First, the effect of the yttria content was studied with the other factors, with the temperature kept constant at 1200°C. It is clear from Figure 1 that there are two crystalline phases; monoclinic phase which is the major phase and tetragonal phase as the minor phase. Two intense peaks ($\bar{1}$ 1 1) and (1 1 1) of monoclinic phase in space group $P2_1/c$, observed at ca.28 and 31.7 2theta are shifted due to misalignment of the sample. Diffraction peak (1 1 1) of tetragonal phase in space group P4$_2$/nmc appeared at ca.30 2theta, which is also shifted from the original peak indicates the stabilization of zirconia after addition of yttria.

Peaks characterizing tetragonal phase in space group P4$_2$/nmc and cubic phase in space group Fm3m are overlapping. It could explain the difference observed on the splitting of (2 0 0) XRD peak into two peaks almost at the same position [16].

It is also clear that all the peaks in the XRD trace are sharp because of the large crystallite size of the micron range size, which results from the annealing process at high temperature. These kinds of processes are known to increase the atomic arrangement in long order crystals. It’s also known that the relatively small atomic scattering factor of oxygen makes it difficult to distinguish with XRD between the cubic and tetragonal phases of YSZ near the phase boundary (8-10 mol% Y_2O_3) [17].

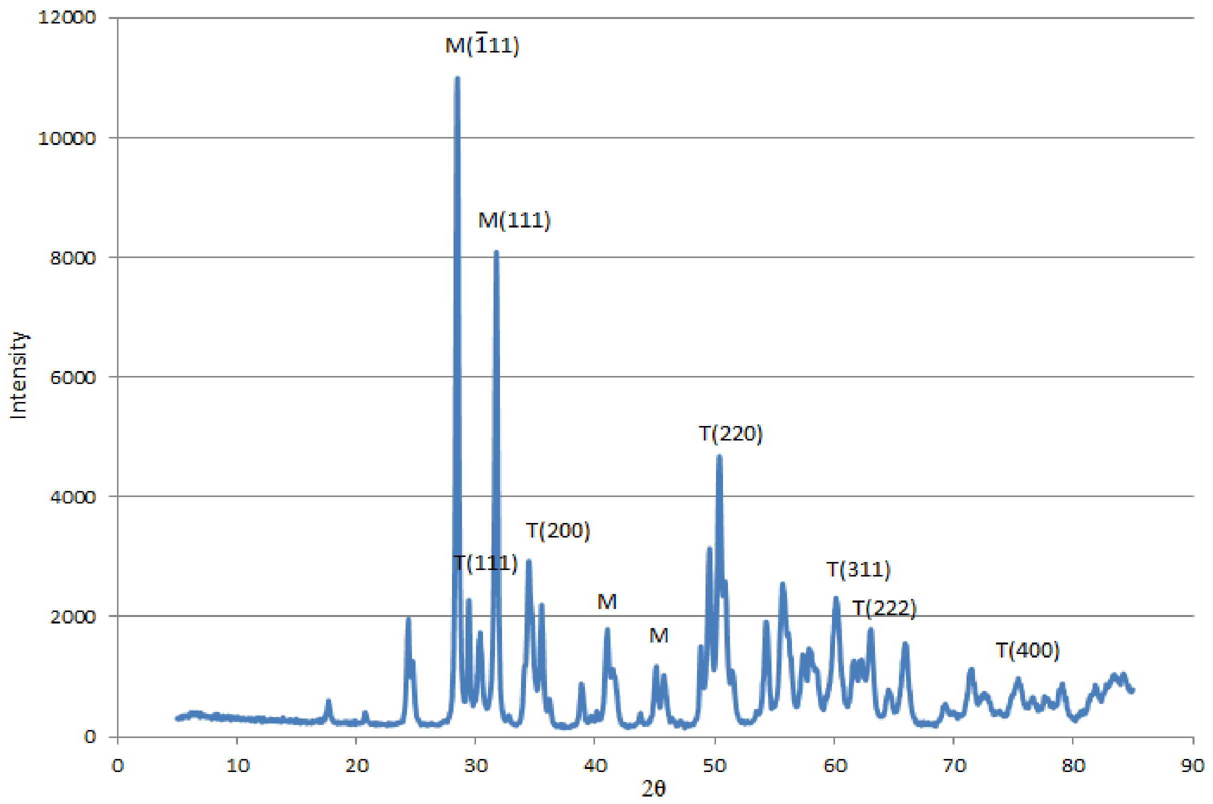

Figure 2. XRD pattern of YSZ sintered at 1200°C (Y_2O_3 content: 8 wt. %)

Figure (2) shows the XRD pattern of the sample after sintering at 1200 °C with increasing the yttria content to 8 wt.%. Although both monoclinic and tetragonal phases can be detected, there is a clear increase in the intensities of the diffraction peaks ($\bar{1}$ 1 1) and (1 1 1) between 28 -31 2 theta. This more likely due to the formation of the cubic phase [18]. Comparison of the diffraction peaks in the above two figures indicates that the intensity of both monoclinic and tetragonal peaks varied with the change of yttria content due to the formation of the YSZ.

3.1.2. Morphology changes with the temperature and yttria content:

Scanning electron microscope images confirm the presence of agglomerates in all samples. Agglomeration takes place as a result of the particles sintering together in order to reduce the surface energy.

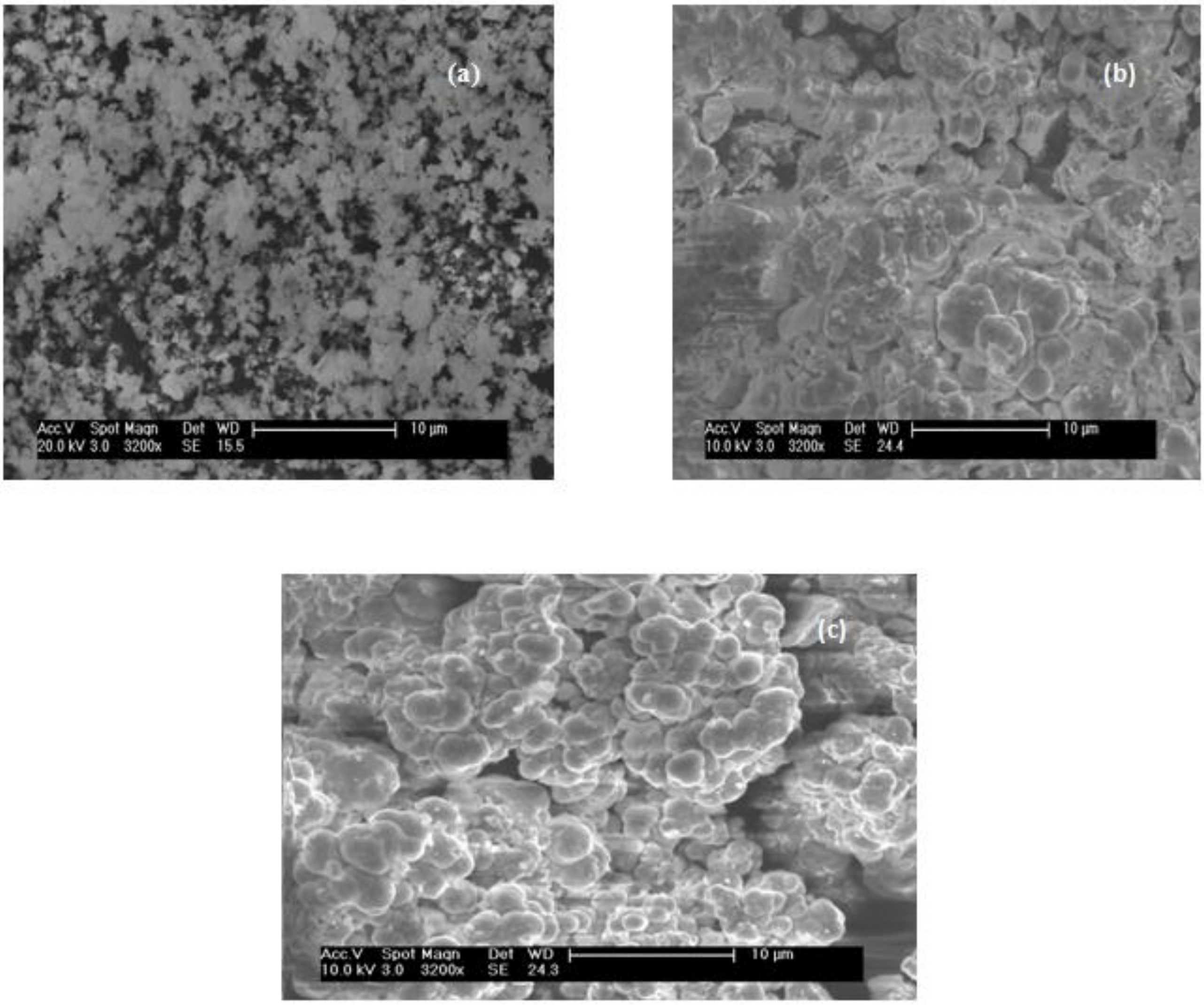

Figure 3. SEM images of YSZ powders with yttria content 8 wt. % sintered; a) at 800°C, b) at 1000°C and c) at 1200°C.

SEM micrograph of the sample after heating at 800°C (Figure 3a) confirms the presence of agglomerates of snow-flake particles with different sizes in the micro scale, while that of the particles after heating at 1000°C (Figure 3b) shows more uniform particles and combined in large cluster because of the surface energy which is the energy resulting from breaking of bonds between atoms at the surface. In Figure 3c (after heating at 1200 °C) more clusters are formed and composed of more agglomerated particles. More surface energy was given by increasing the annealing temperature. It's observed that particles became more uniform and more agglomerated as a function of temperature.

Figure 4 depicted the effect of the Y_2O_3 content on the morphology of the YSZ. Particles are agglomerated into clusters with each cluster composes of approximately 10 to 20 particles ranges in size from 20-50μm composed of particles of about 2μm in size. The particles are combined in large clusters because of the surface energy and the particles become sphere in shape and more uniform.

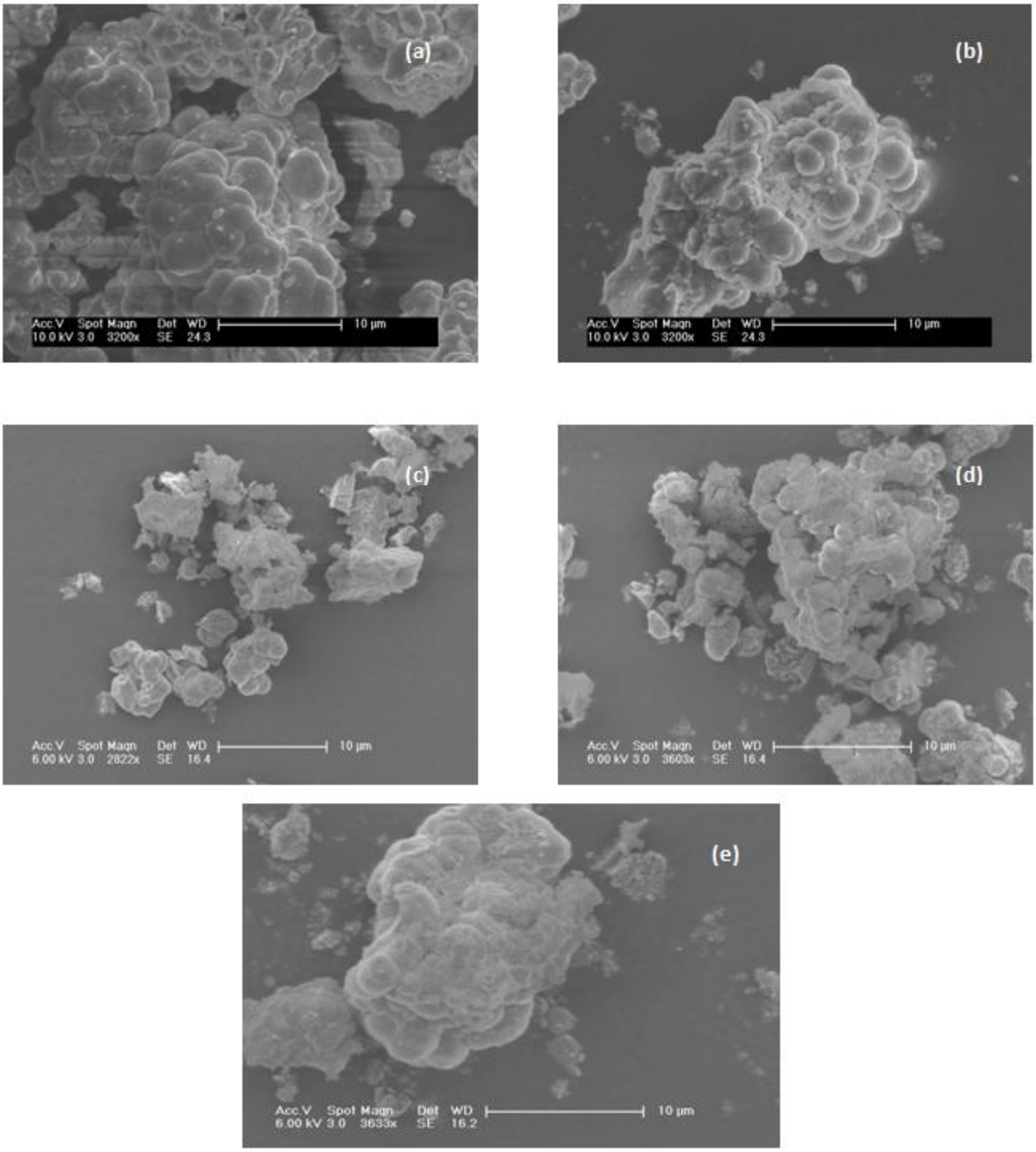

Figure 4. SEM micrographs of YSZ powder sintered at 1000°C as a function of yttria weight content; a) 6%, b) 8%, c) 10%, d) 15% and e) 20%.

It’s well known that ionic radius of zirconium ion is 0.82 Å and that of yttrium ions is larger (0.96 Å) [19]. When doping ZrO_2 with Y_2O_3, it’s expected that the difference in the ionic radius causes some disturbance in the long range crystallinity of the zirconia particles. As the yttria content increased to 10 wt. % (Figure 4c) particles are not uniform, sharp edges result from internal cracks due to doping with different size ion, also the particles are semi-faceted and all the particles seems to be very refractory in nature and tend not to sinter together, this is expected from a refractory ceramic like YSZ which have melting point exceeding 2760°C. There is a slight charging in the SEM micrograph (Figure 4d) that even the gold coating didn’t reduce it due to the sintering of particles together in very big agglomerate. Figure 4e shows large agglomerates, inhomogeneity in particle shape and particle size increased from 1μm to 3μm due to increase in yttria content.

3.1.3. Electric conductivity of YSZ sintered pellets:-

Electric conductivity results have shown that conductivity increase as the yttria content increase.

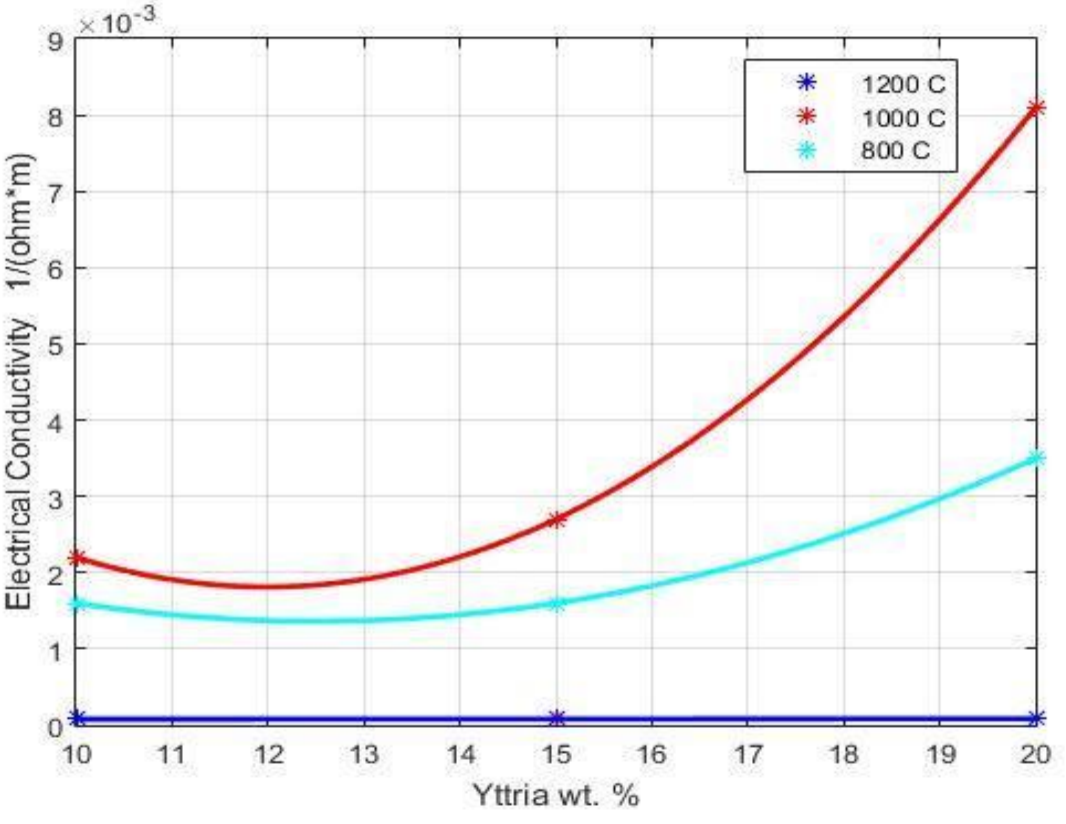

Figure 5. A comparison between the electric conductivity of YSZ samples sintered at 800°C, 1000°C and 1200°C.

Figure 5 shows a comparison of the electric conductivity between YSZ samples sintered at 800˚C, 1000°C and 1200°C. At all the yttria content, the sample heated at 1000°C has higher conductivity than those sintered at 800 °C and 1200˚C. It shows a significant decrease in the electric conductivity of YSZ samples sintered at 1200 °C as compared to those sintered at 800˚C and 1000°C to be 7.89*10^{-5}, 8.05*10^{-5} and 8.45*10^{-5} $\Omega^{-1}m^{-1}$ for yttria weight content 10%, 15% and 20% respectively. This may be due to the volume expansion and shape deformations, which occur through the martensitic effect of tetragonal to monoclinic transformation [20]. Such transformation can be observed in the phase diagram by Scott [21]. This large volume setup large strains in the structure which cannot be relieved by diffusion instead they are accommodated by elastic or plastic deformation of the surrounding matrix. This volume expansion causes no sufficient vacancy site mobility and thus reduces the oxygen vacancies responsible for permitting YSZ to conduct the electric current. It can be concluded that the optimum conditions for preparing YSZ are 20 wt. % of yttria content and sintering at 1000 °C.

3.2. Preparation of YSZ using zirconia produced from natural zircon:

By Using the optimum conditions obtained from the previous section i.e. yttria content 20 wt. % and sintering at 1000^{o}C for 2 hours, YSZ is prepared from zirconia obtained from natural zircon by the same procedure described elsewhere [15].

3.2.1. Phase identification of zirconia by XRD:

To identify the phases present in the obtained zirconia from natural zircon, the sample was subjected to XRD analysis and the obtained pattern is illustrated in Figure 6. This XRD pattern confirms the presence of both tetragonal and monoclinic phases for zirconia prepared after the oxychloride treatment. By comparing this result with that of zirconia prepared after the basic sulphate treatment [14], there was no phase change of tetragonal to monoclinic during calcination.

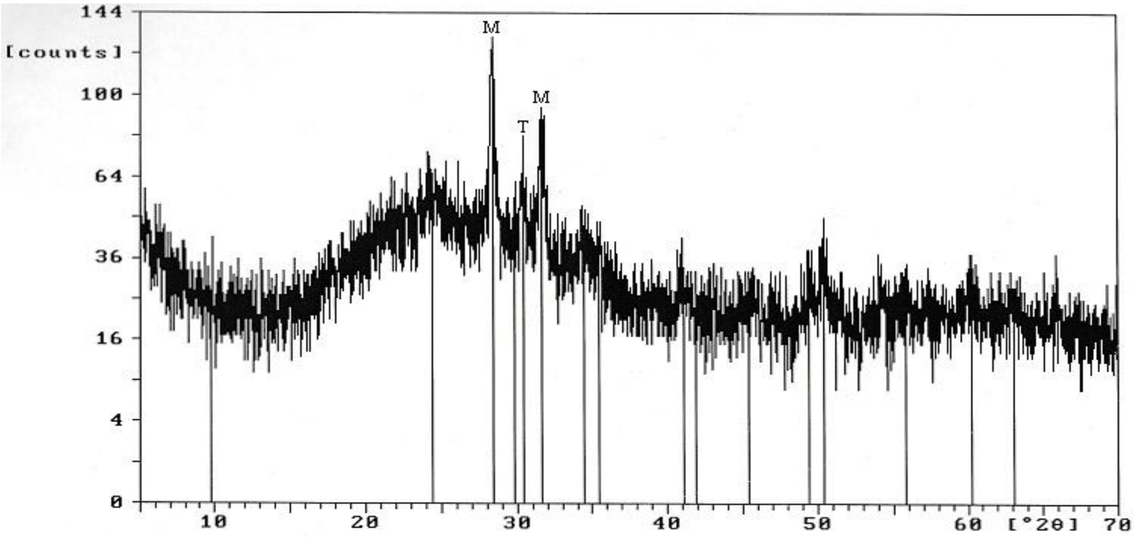

Figure 6. XRD pattern for the obtained zirconia from natural ore after the oxychloride treatment.

3.2.2. Impurities determination by XRF analysis:

Table 1. XRF Analysis for the obtained zirconia

Component	**XRF analysis for the obtained zirconia (ppm)**
	Zirconyl chloride treatment
Fe	< 50
Ti	512
Mg	98
Ca	85
Na	65
K	74
U	< 10
Th	< 10
SiO_2	489
$ZrO_2 + HfO_2$ %	99.86

The obtained zirconia through oxychloride treatment was subjected to XRF analysis to determine the level of impurities. Table (1) shows the presence of impurities of different elements with ionic radius, which may affect the electric conductivity of the yttria stabilized zirconia prepared using zirconia obtained from natural ore.

3.2.3. Electric conductivity of YSZ prepared using zirconia obtained from natural ore:

The electric conductivity result obtained for YSZ sample containing 20 wt. % of yttria and sintering at 1000 °C for 2 hours was $8.42*10^{-5}\ \Omega^{-1}m^{-1}$.

This value is much lower than that obtained for YSZ sample prepared from synthetic yttria and zirconia under the same conditions ($8.04*10^{-3}\ \Omega^{-1}m^{-1}$). This marked decrease in the case of the former YSZ sample may be due to the presence of a high level of impurities of quaternary oxides e.g., Ti, Si and Fe oxides which reduce the concentration of oxygen vacancies responsible for permitting YSZ to conduct O^{2-} ions and thus conduct the electrical current. So there is no sufficient vacancy site mobility. Moreover, the impurities such as TiO_2 and SiO_2 are of refractory elements which have low electric conductivity are present with high concentrations i.e., 512 and 489 ppm respectively, which replaced some of the Zr^{4+} and Y^{3+} in the lattice and thus decreases the vacancy site mobility and hindrance of the electric current conduction.

4. CONCLUSION

The present work studies the effect of sintering temperature and yttria weight content on the preparation of YSZ from synthetic Y_2O_3 and ZrO_2. The optimum conditions found to be 20 % yttria weight content and sintering at 1000 °C to obtain the best electric conductivity and morphology results. These conditions were applied to prepare YSZ using zirconia prepared from natural ore and synthetic yttria. The electric conductivity value was decreased for YSZ due to the effect of impurities present in zirconia prepared from natural ore.

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