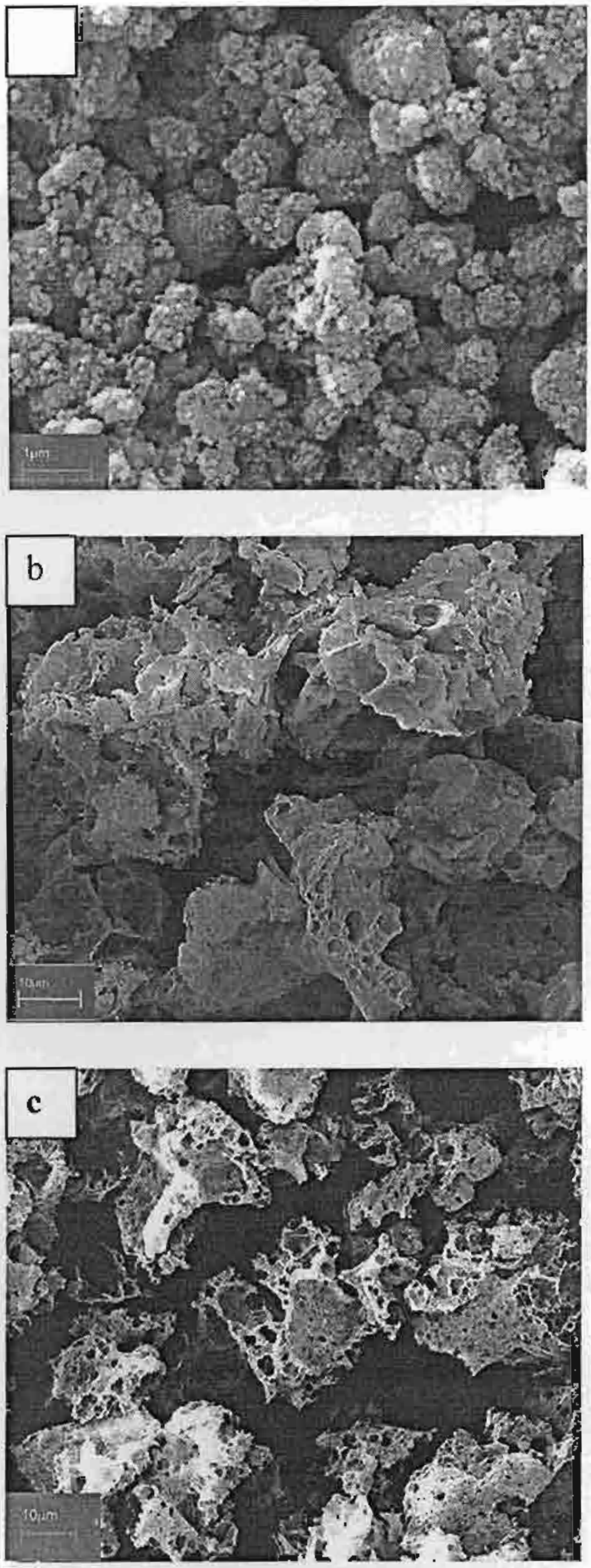

Figure 4.1. (a) As received zirconia powder with a raspberry morphology (b),(c) MAT-diol and Y-diol fired at 700 °C for 1 hour

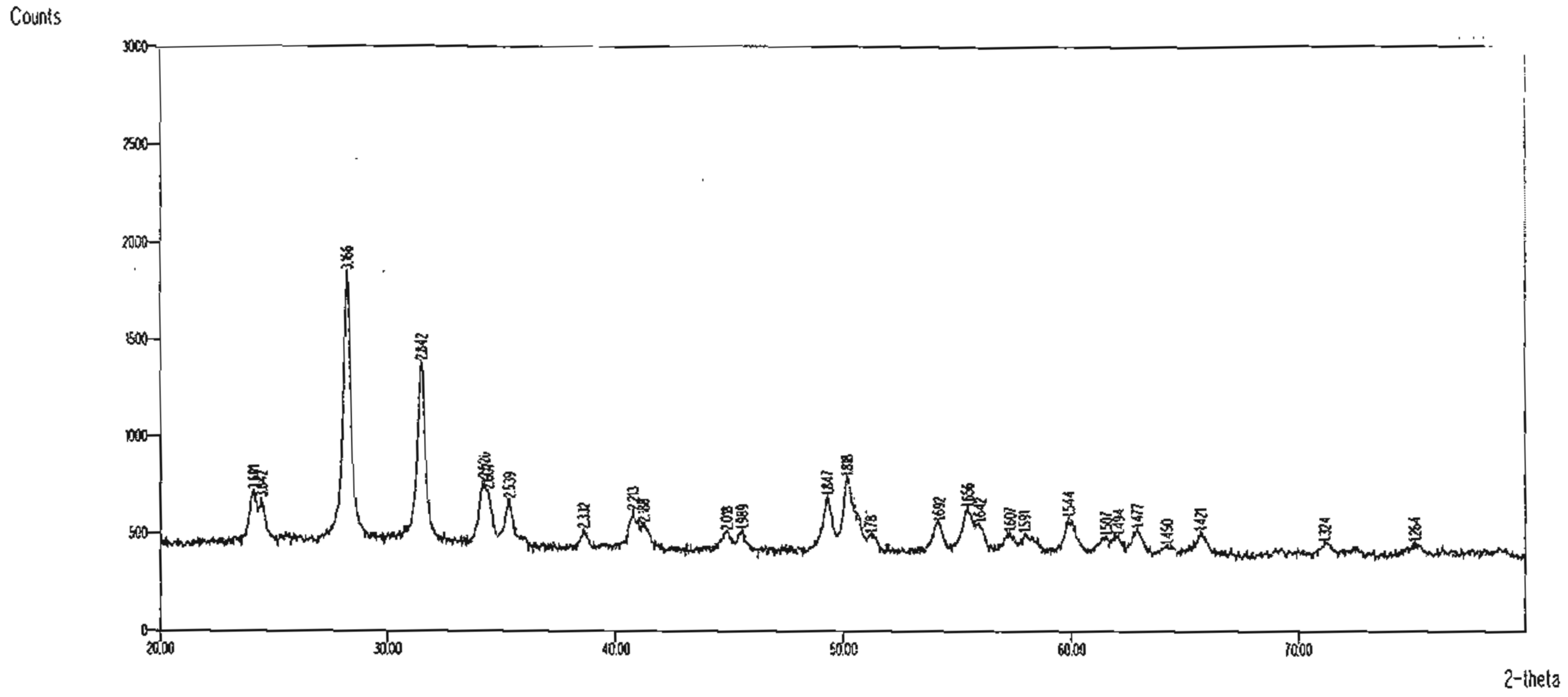

Figure 4.2. XRD pattern of the as received zirconia powder which indicates the monoclinic structure.

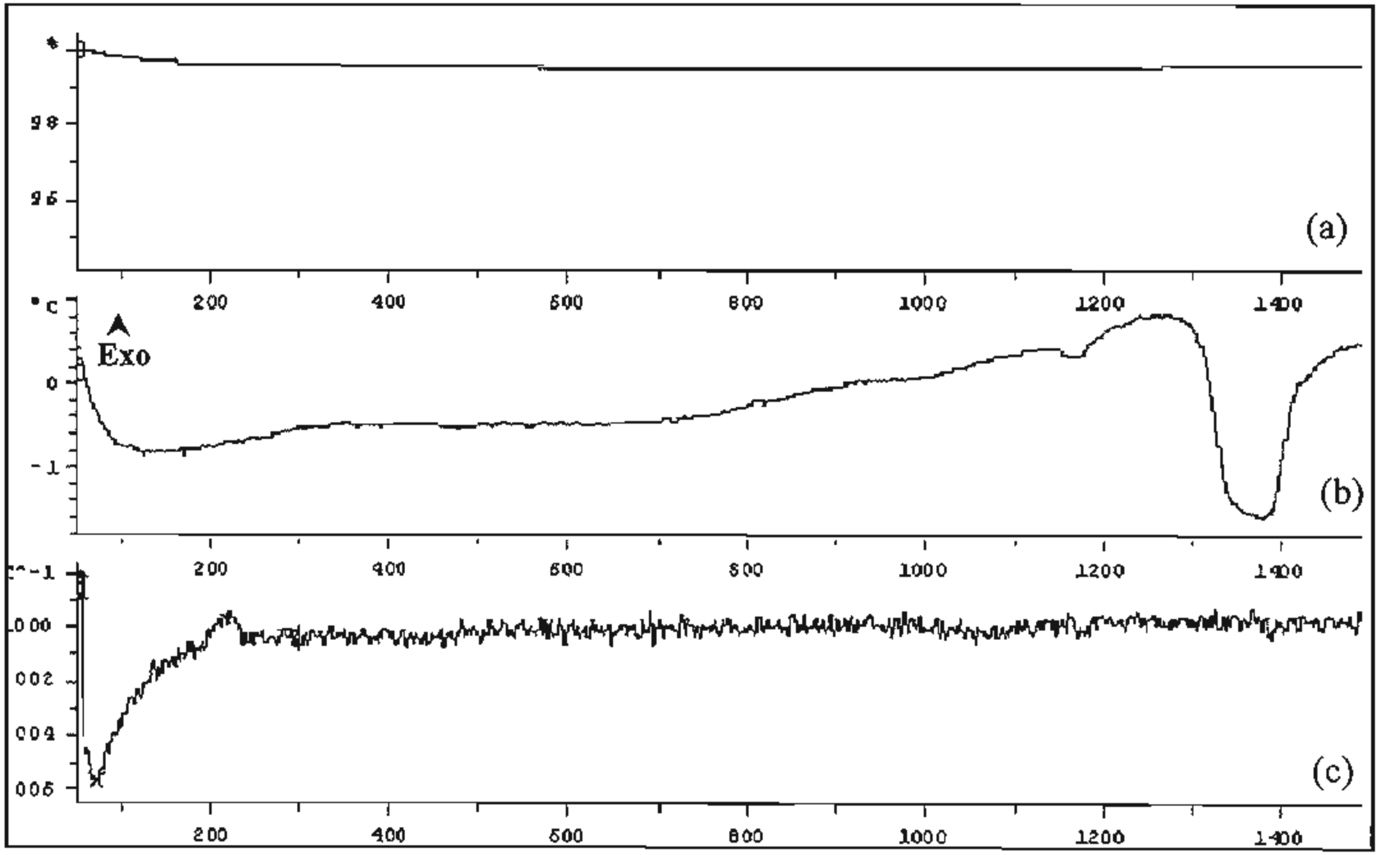

Figure 4.3: (a) TGA, (b) DSC and (c) DTG for the as received ZrO_2 powder.

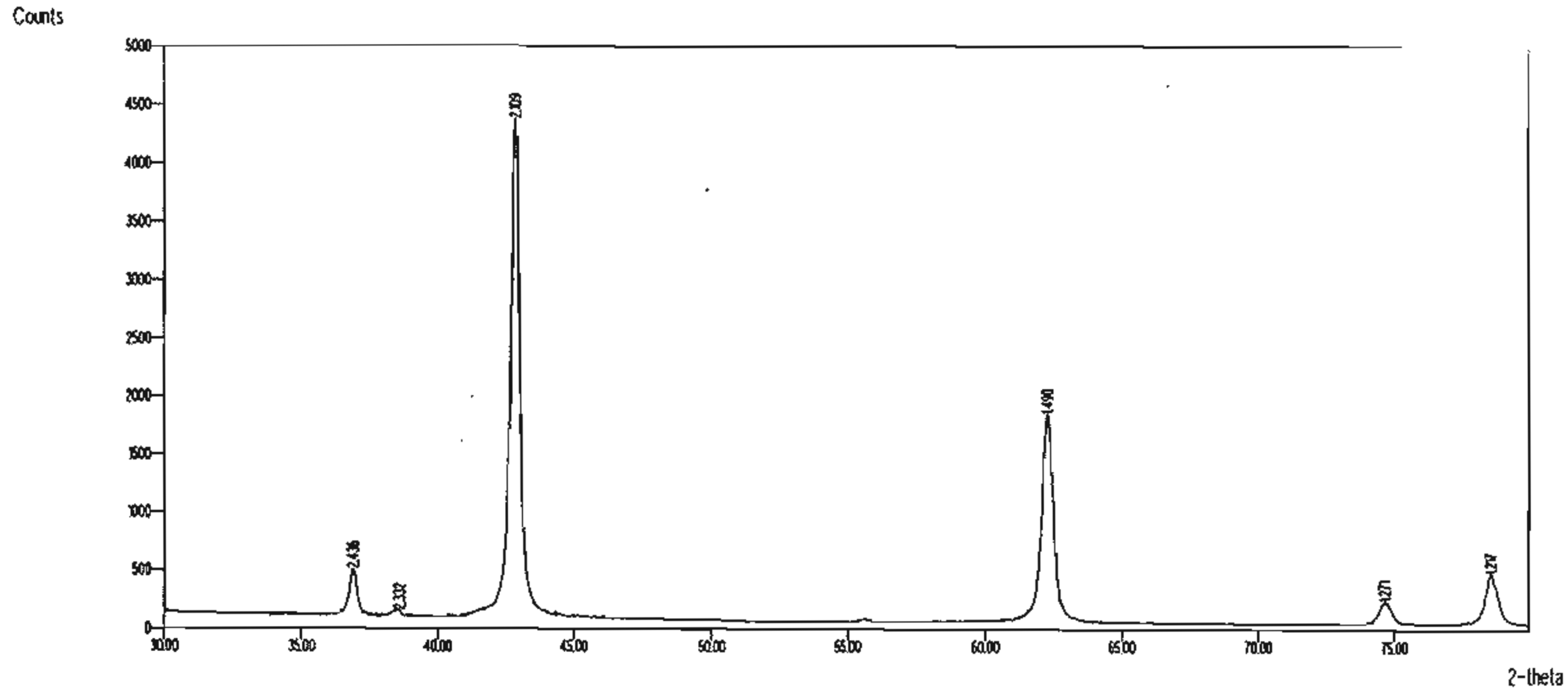

Figure 4.4(a). XRD pattern for the MAT-diol gel fired at 700 °C for 1 hour.

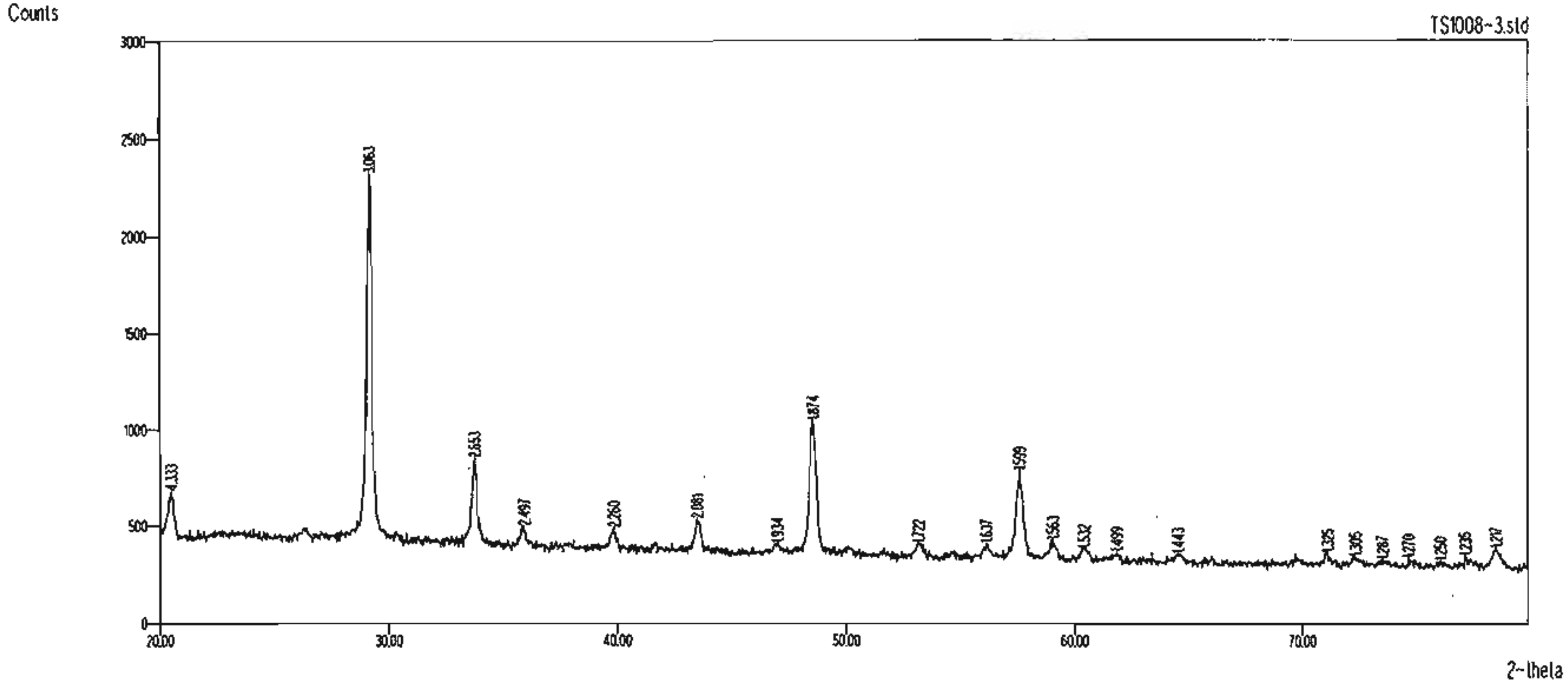

Figure 4.4(b). XRD pattern for the Y-diol gel fired at 700 °C for 1 hour.

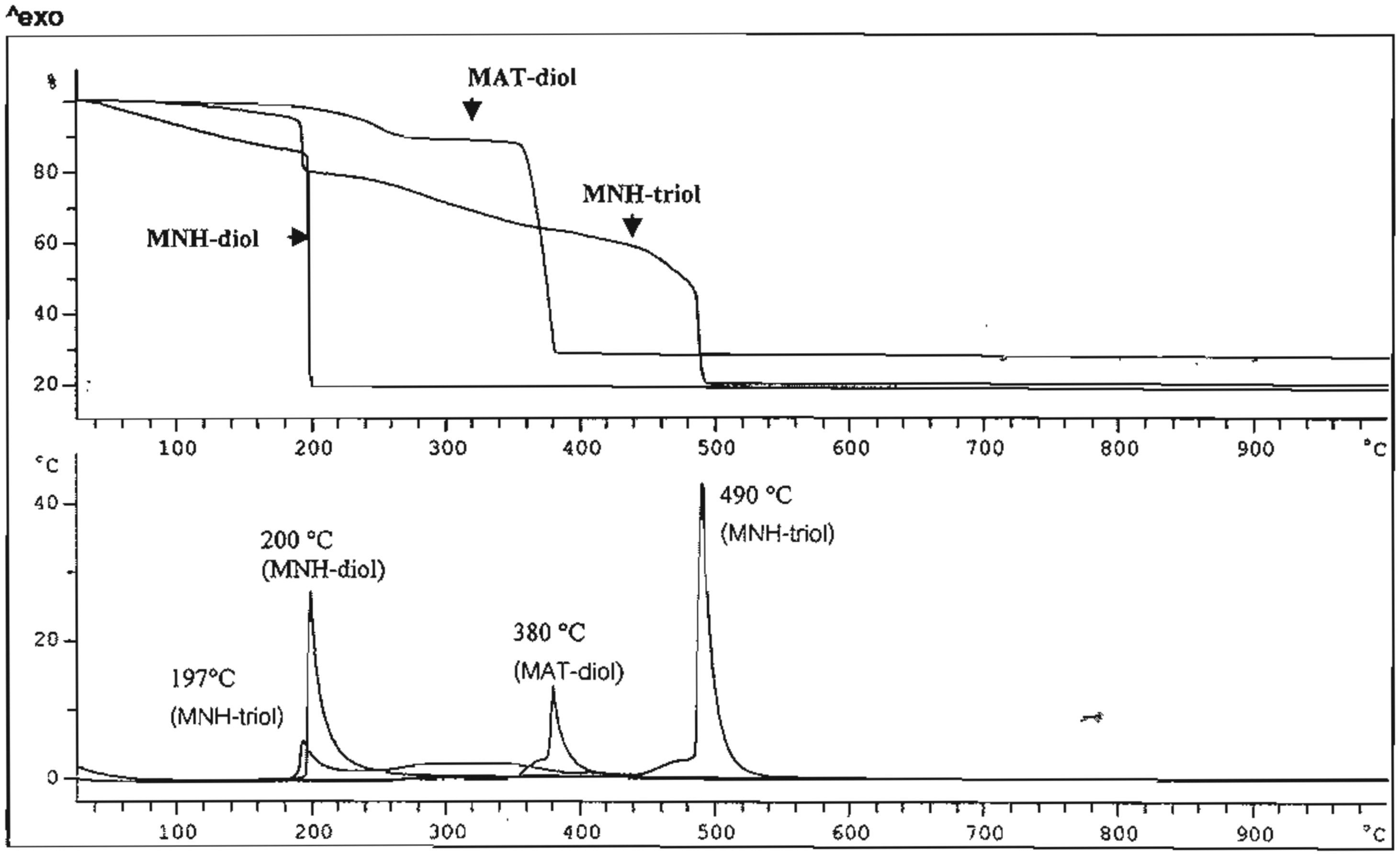

Figure 4.5: TGA/DTA curves for dried gel powders. The powders were heat treated from room temperature to 1000 °C with the heating rate of 20°C/minute in air atmosphere.

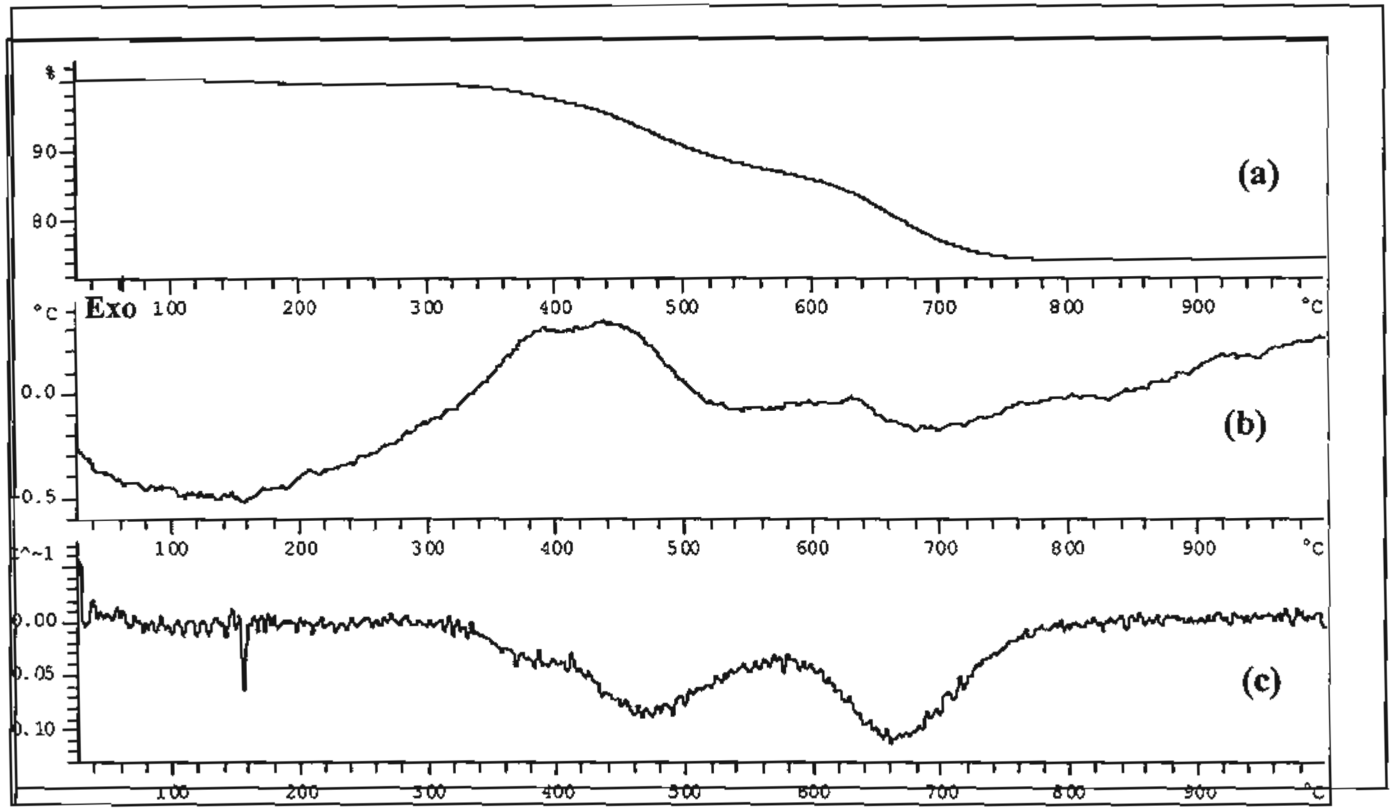

Figure 4.6: (a) TGA, (b) DSC and (c) DTG for the as received Y_2O_3 gel powder.

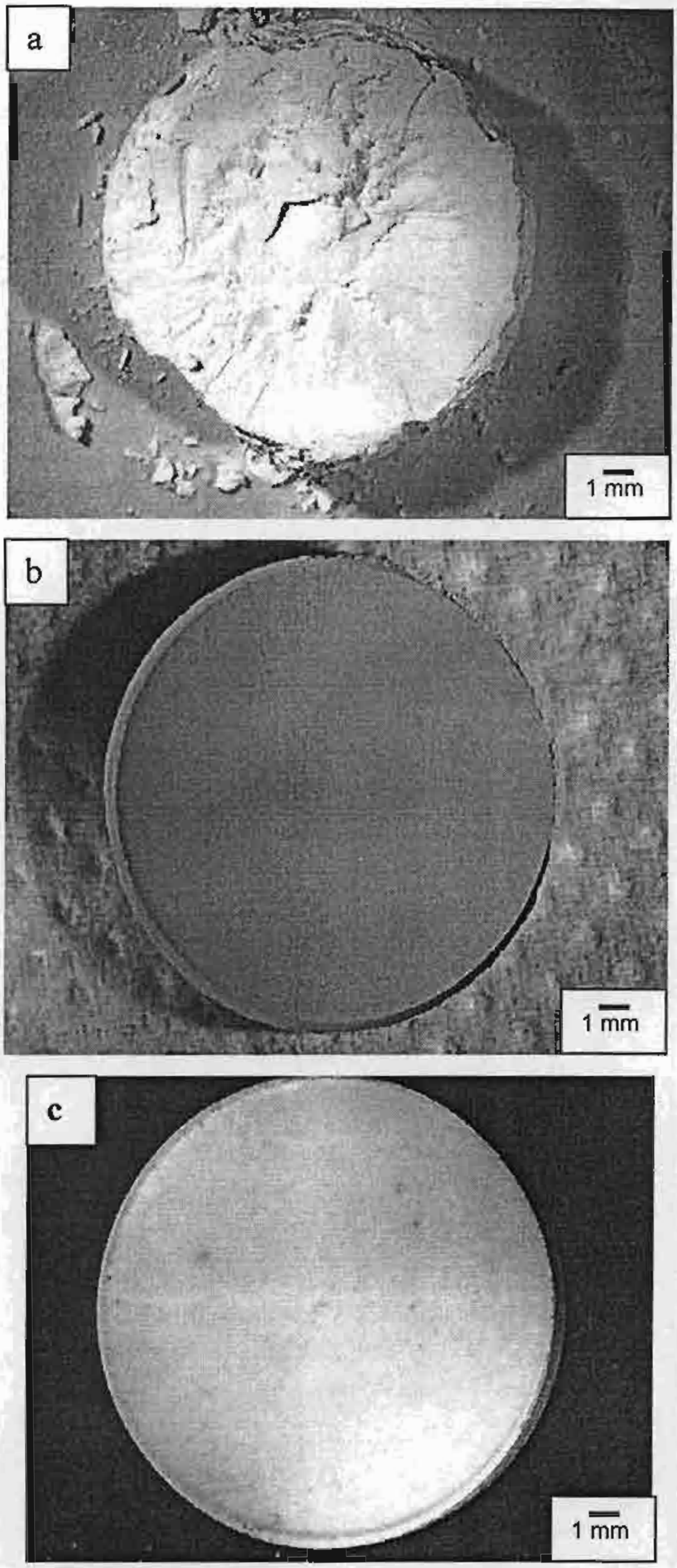

Figure 4.7: A comparison between compaction of three zirconia powders sieved through 120 nylon mesh (a) as received powder (b) yttria sol-coated powder and (c) magnesia sol-coated powder.

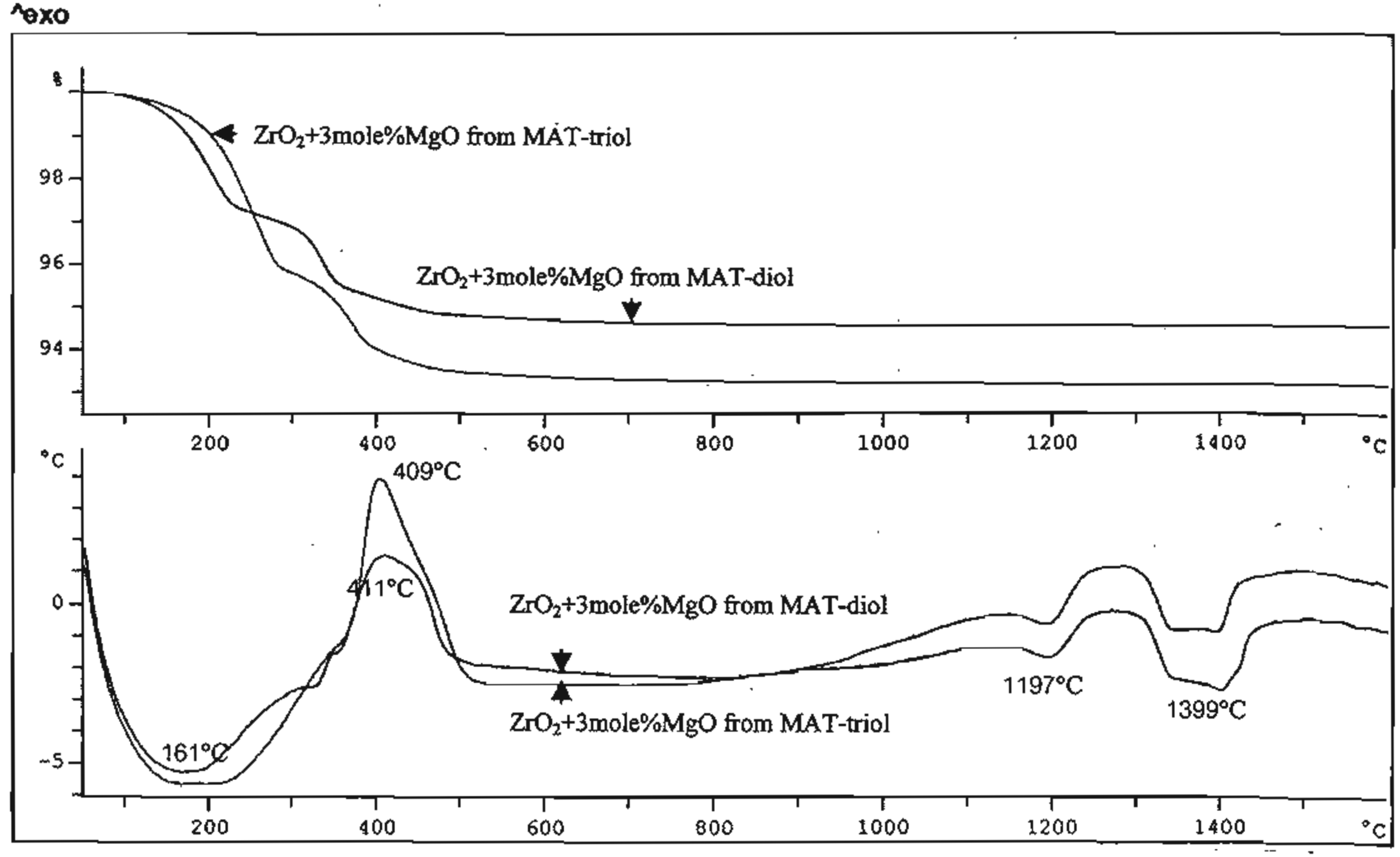

Figure 4.8: TGA/DTA curves for pellets of ZrO_2 +3 mole% MgO derived from MAT-diol and MAT-triol sols. The powders were heat treated from 50 °C to 1600 °C with the heating rate of 20°C/minute in air atmosphere.

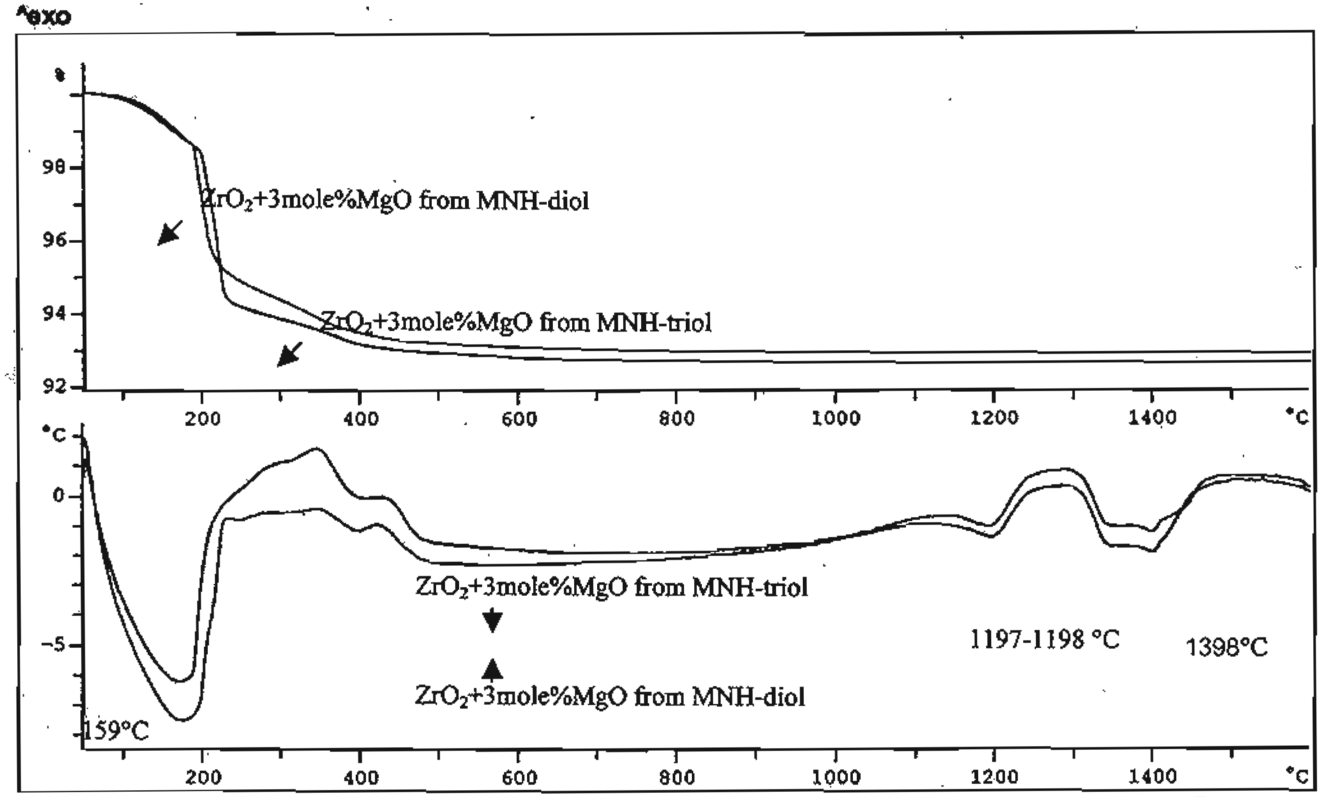

Figure 4.9: TGA/DTA curves for ZrO_2 +3 mole% MgO derived from MNH-diol and MNH-triol sols. The powders were heat treated from 50 °C to 1600 °C with the heating rate of 20°C/minute in air atmosphere.

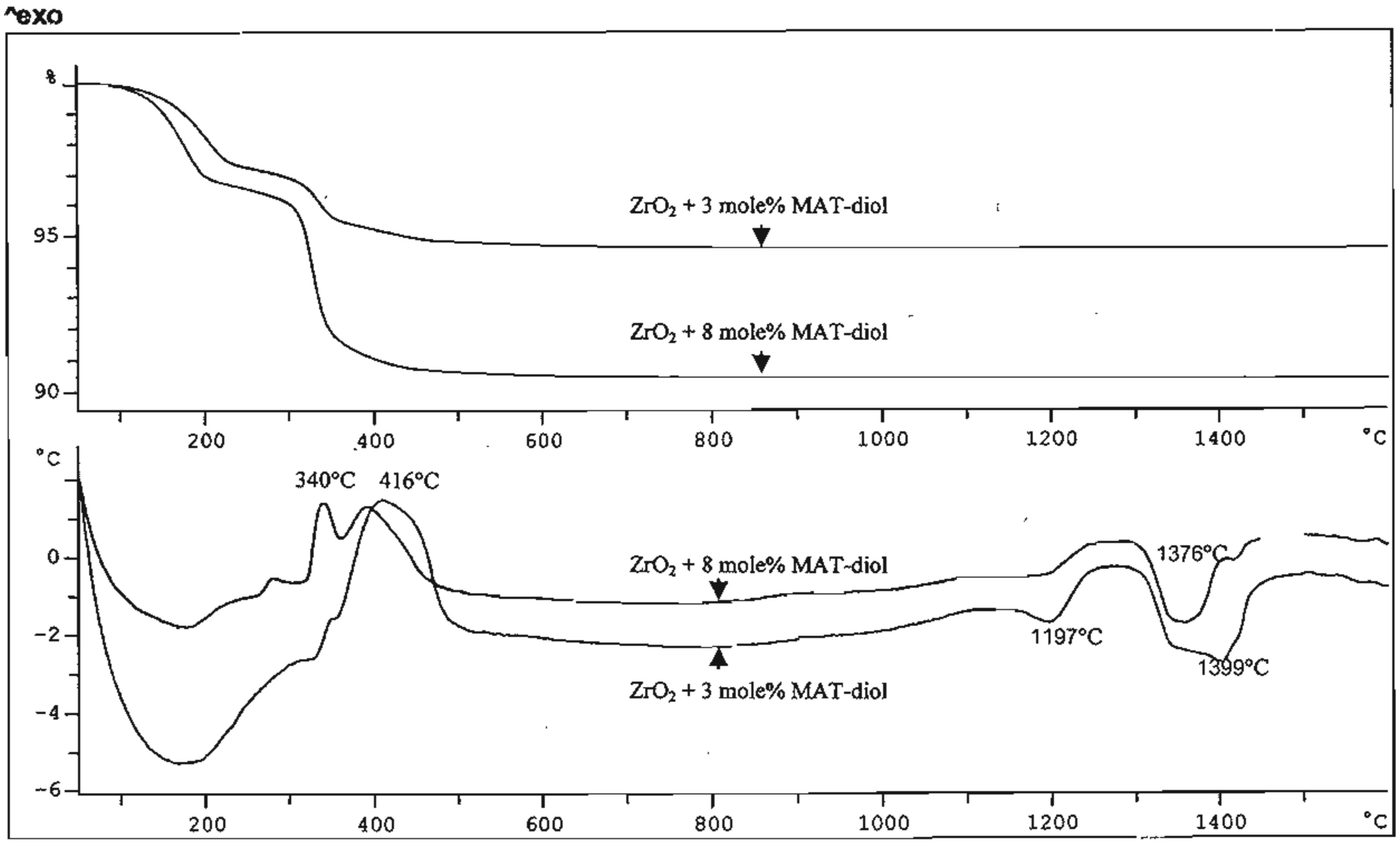

Figure 4.10: TGA/DTA curves for ZrO_2 + 3 and 8 mole% MgO derived from MAT-diol sols. The powders were heat treated from 50 °C to 1600 °C with the heating rate of 20°C/minute in air atmosphere.

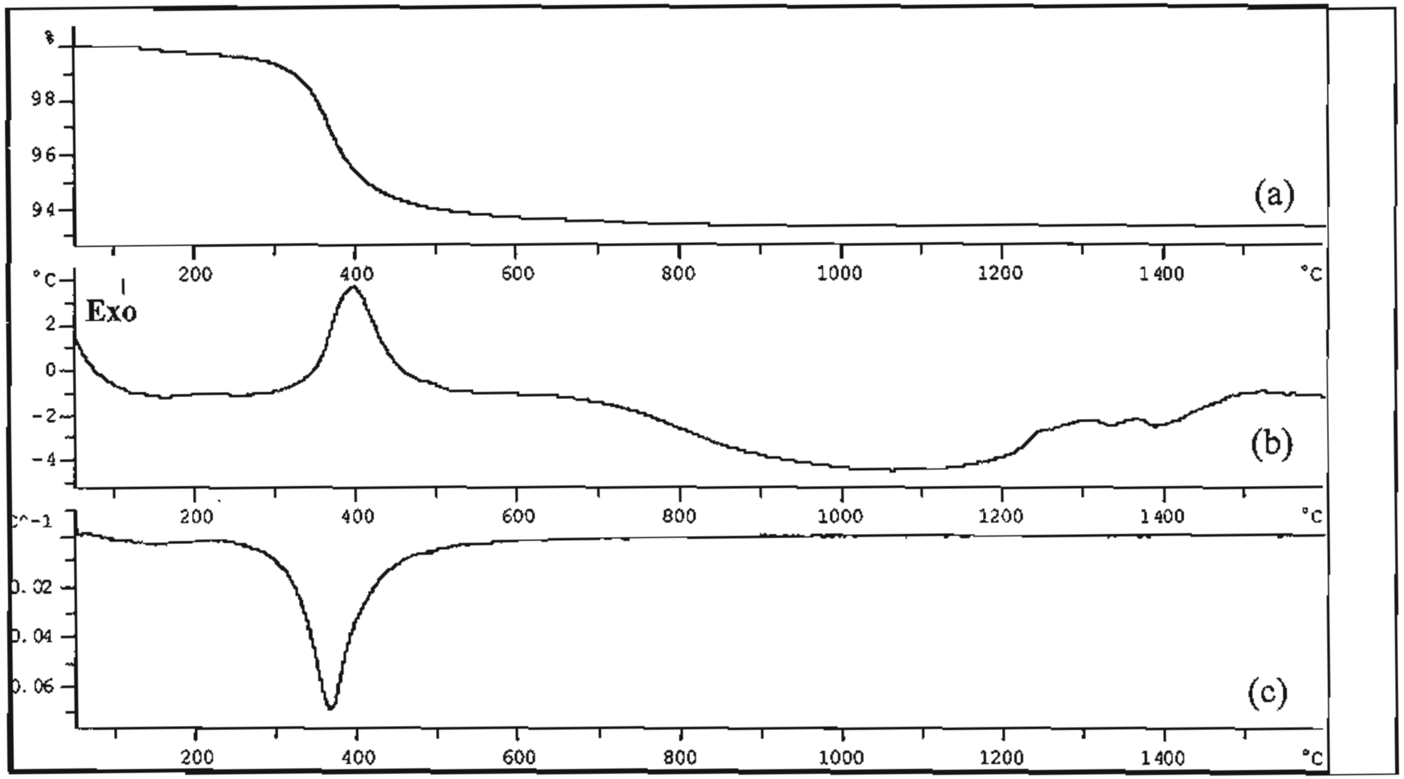

Figure 4.11. (a) TGA, (b) DSC and (c) DTG for the Y_2O_3 sol-coated ZrO_2 powder.

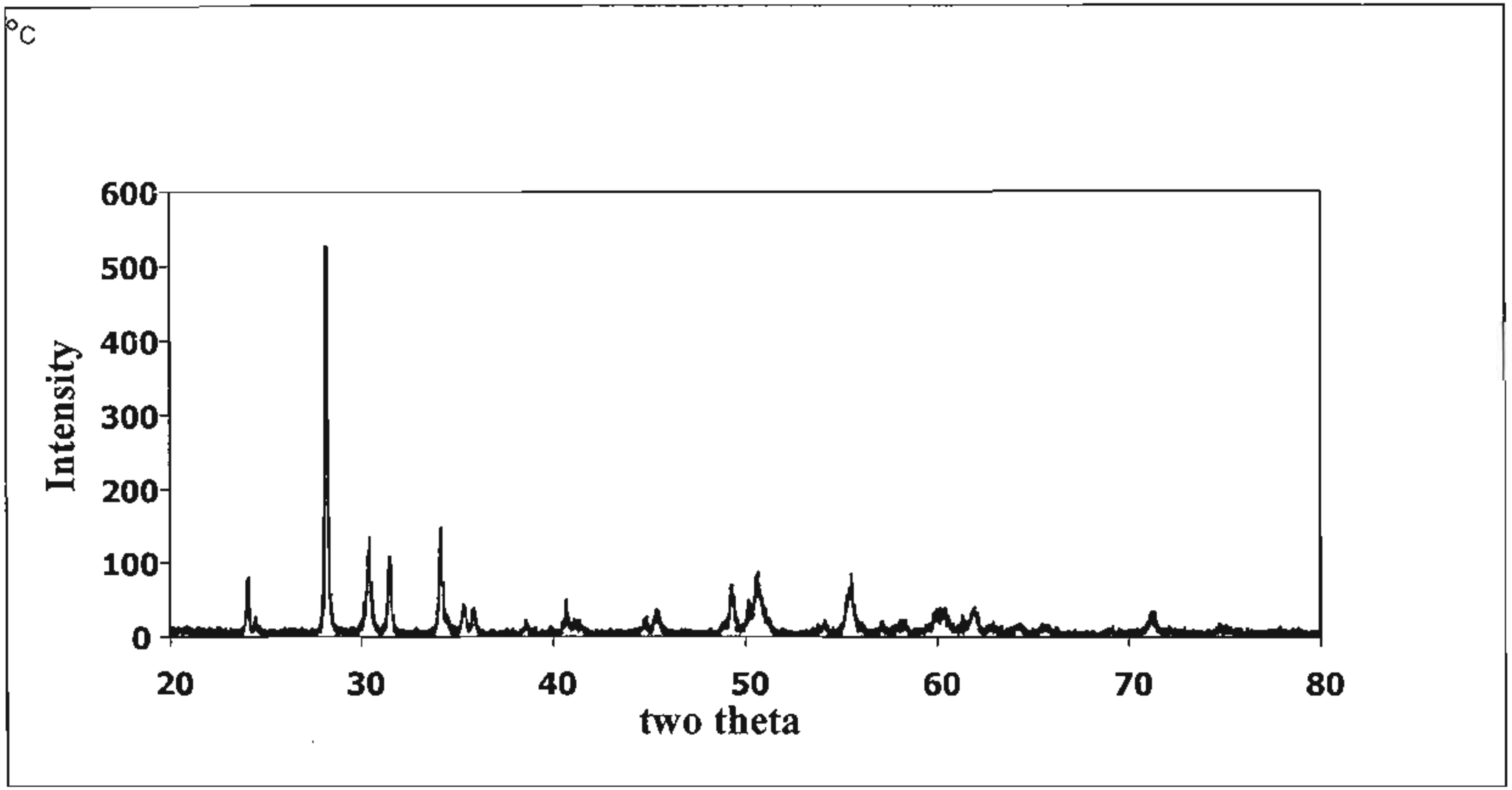

Figure 4.12 XRD pattern for the 8 mole% magnesia doped zirconia specimen sintered at 1600 °C for 8 hours.

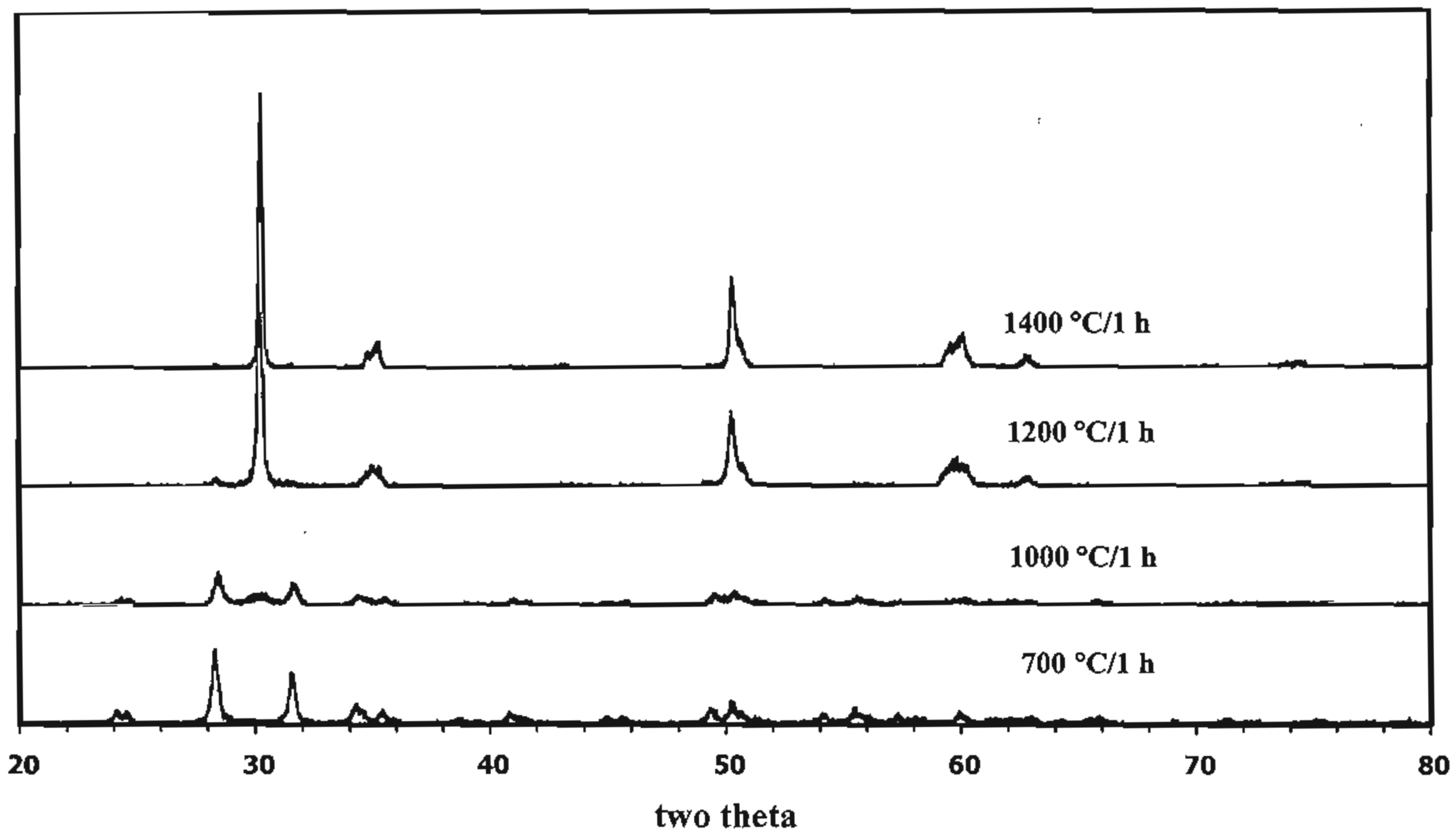

Figure 4.13: XRD results for the Y_2O_3 sol-coated-ZrO_2 powder fired at various temperatures. The powder fired at 700-1000 °C are mainly monoclinic while the powder fired at 1200-1400 °C are mainly cubic/tetragonal phases.

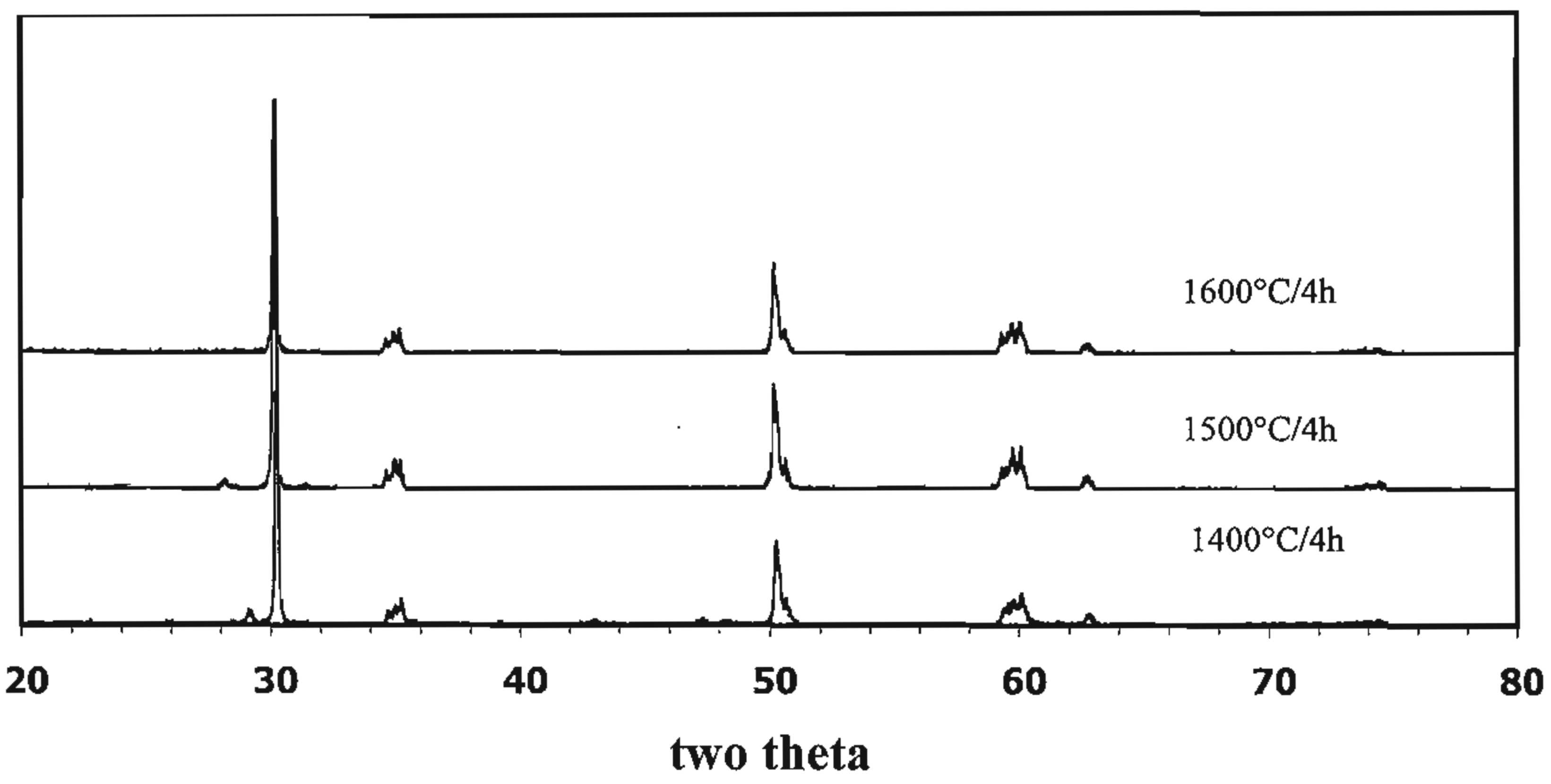

Figure 4.14: XRD patterns for the samples sintered for 4 hours at 1400-1600°C.

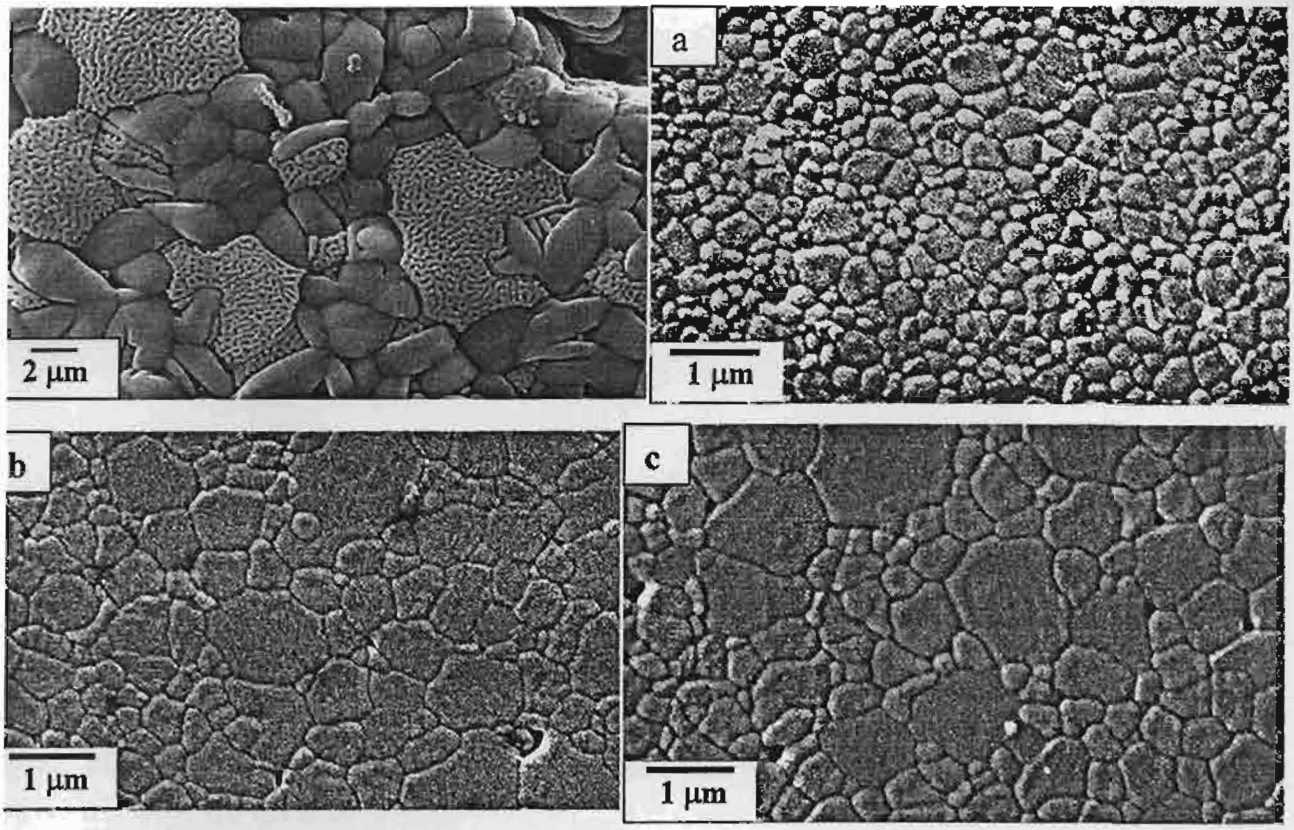

Figure 4.15: SEM micropgraphs of (a) the 8 mole% MgO-ZrO_2 sample fired at 1600 °C for 8 hours and sintered sample of 8 mole % Y_2O_3-ZrO_2 samples at (1) 1400 °C, (b) 1500 °C and (c) 1600°C for 4 hours.

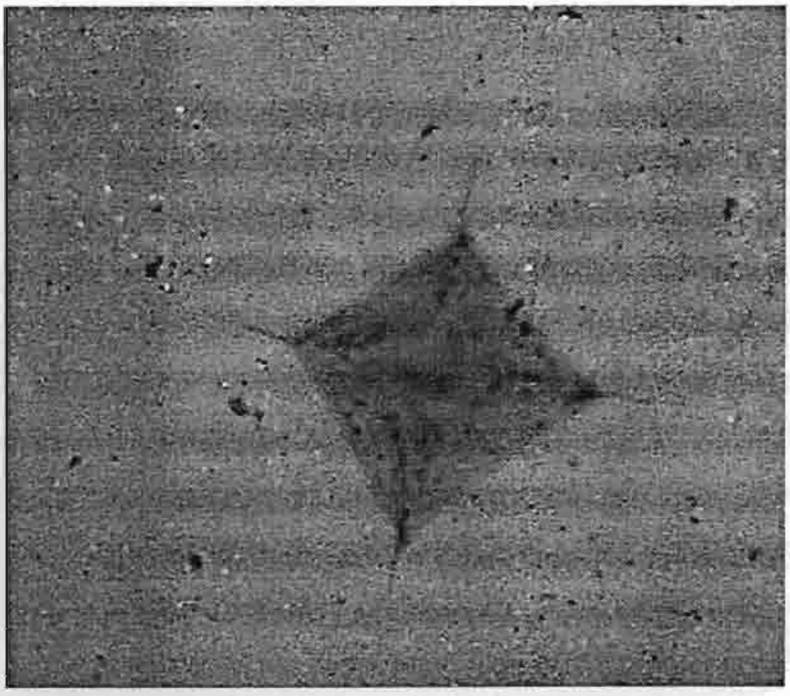

Figure 4.16. The OM micrograph of indent under a load of 2404 mN/10 seconds for the YSZ sample fired at 1600°C for 1 hour.

Conclusion

Magnesia doped zirconia

Four different types of sols have been synthesized in this research. However, only the one prepared using magnesium acetate, glacial acetic acid and 1,3 propane diol as starting reagents which is called MAT-diol has been used to coat onto zirconia powder in this research, mainly due to its best binding ability. The synthesized MAT-diol sol shows that it can be used as a perfect binder since it can tolerate the heating rate as high as 20°C/minute. However, the diffusion of magnesium sol into zirconia powder occurs relatively slow, thus a relatively high sintering temperature ($\geq$1750 °C) is required to obtain a satisfied structure (see MgO-ZrO_2 phase diagram in Chapter 2). Due to the lack of high temperature furnace, firing of compacted specimens is thus performed only at 1600 °C for 8 hours. The sintered samples show a phase separation due to a relatively low firing temperature and contain mainly monoclinic phase as indicated using an XRD technique. A more proper firing condition is needed for further investigating this system.

Yttria doped zirconia

Two different types of yttria sols have been synthesized but the one that has been employed as a source of phase stabilizer and binder in this research is called Y-diol in which yttrium nitrate hexahydrate, methoxyethanol and 1,3 propanediol are used as starting reagents. Although the binding ability of the yttria sol is inferior to that of the magnesia sol, it is a superior phase stabilizer i.e. diffusion of yttria into the zirconia powder occurs at a much lower temperature. This is due to three reasons; the high surface area of the zirconia powder and also the yttria gel as well as the relatively high diffusion rate of yttria in the zirconia lattice. The XRD results shows that stabilization of the monoclinic zirconia power in the tetragonal/cubic forms have already achieved at the temperature as low as 1200 °C. Traditionally stabilized zirconia has been prepared using a co-precipitation technique in which a phase stabilizer is distributed uniformly in zirconia crystals. Thus the sol-coated powder technique is an alternative method for preparation of stabilized zirconia in which concentration gradient may be needed. Besides, this technique requires a relatively simple apparatus setup and particle size reduction is not required.

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The Use of Metal Oxide Sols as Dopants and Binders in Zirconia

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Abstract

Air-stable magnesia and ytttria sols have successfully been synthesized and mixed with zirconia powder using a simple mixing and stirring technique. The coating sols showed a dual functions; as a binder and a phase modifier. Specimens prepared with additions of sols showed far superior green strength and sinterability in comparision to those formed without addition of sol or binder. Thermal analysis and XRD of the dried magnesia and ytttria gel powders indicated that they had already crystallised into oxides at the temperature below 700 °C. Specimens coated with 8 mole% MgO then fired at 1600 °C for 8 hours exhibited a phase separation, indicating that the heat treatment schedule must be modified to obtain the more proper structure. XRD result revealed that the dominant phase in this specimen was monoclinic with a less amount of tetragonal and cubic phases. In contrast, diffusion of coated yttria sol into the zirconia powder seemed to occur at lower temperature since the specimens fired at 1200 °C only for 1 hour exhibited three crystalline phases, monoclinic, tetragonal and cubic in which cubic and tetragonal are the major phases. A bi-modal structure of tetragonal and cubic phases was generally observed under an SEM in this system.

Keywords : zirconia, magnesia, yttria, sols.

1. Introduction

Zirconia (ZrO_2) is one of the most interesting ceramic materials which is attributed to a unique set of its properties. It is a prime candidate for structural applications because of superior strength, toughness, and wear resistance. It is ionically conductive above 600 °C, and in the cubic form is widely used as an oxygen sensor.

Pure zirconia undergoes a number of reversible phase transitions during heat treatment but the most destructive is the transformation from tetragonal-*(t)* to monoclinic-*(m)* on cooling below 1270°C. Since the monoclinic phase has about 3-5% larger volume than the tetragonal phase, zirconia is invariably subjected to cracking thus making exploitation of zirconia ceramic impossible without structural stabilisation. To stabilise the high temperature phases at room temperature, in order to avoid this deleterious problem, CaO, CeO, Y_2O_3 or MgO are usually added to zirconia in appropriate proportions .

Different methods such as plasma synthesis, co-precipitation, hydrothermal precipitation and sol-gel processing have been utilized for preparation of stabilized zirconia [5-7]. The main defects of these methods are compositional inhomogeneity in powder products, a requirement for complicated equipment, or difficult experimental procedures.

In this research, the authors have proposed a novel technique for preparation of stabilized zirconia ceramics by a simple sol-powder coating. The magnesia (MgO) and yttria (Y_2O_3) sols have been synthesized at normal atmosphere and mixed with a zirconia powder under a stirring condition. The adding sols function as a polymeric binder to promote densification and phase modifiers to stabilize zirconia in desired structures.

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2. Experimental Work

The zirconium oxide powder used in this research was donated by MEL Chemicals, Swinton, Manchester, England (Zirconia (ZrO_2)+ Hafnia (HfO_2) was about 99 wt% in which Hafnia accounted for 2% of the total). The as-received powder has the monoclinic structure and has an average grain size reported in the material data sheet of 0.8 μm. However, this reported particle size is actually the size of the agglomerates of powder which could not be broken down during the particle size measurement. The particle size calculated using the equation :$D = 6/\rho A_s$ is equal to 0.05 μm. The Y_2O_3 and MgO sols were prepared using following starting reagents; magnesium acetate tetrahydrate [$Mg(CH_3COO)_2.4H_2O$,99.9%], glacial acetic acid (CH_3COOH), 1,3 propanediol [$HO(CH_2)_3OH$, 98%], yttrium nitrate hexahydrate [$Y(NO_3)_3.6H_2O$, 99.9%], and 2,4 pentanedione $CH_3COCH_2COCH_3$. The sols preparation experiments are schematically illustrated in Figure 1. When synthesized, calculated quantities of magnesia and yttria sols (nominal composition of 8 %) were added to the ZrO_2 powder and kept under a stirring condition at 100 °C until the completely dried sol-powder mixtures were obtained. The resulting powders were then sieved through a 120 nylon mesh and pressed at 50 MPa. Specimens were fired at different conditions and characterized using series of techniques such as TGA, SEM and XRD.

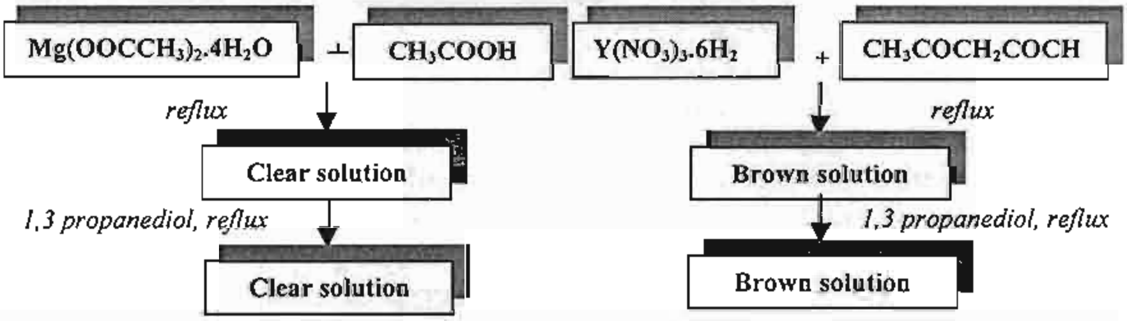

Figure 1: A schematic diagrams for preparation of magnesia (left) and yttria sols (right).

3. Results and Discussion

The zirconia powder used in this research cannot be compacted on its own, whereas the sol-coated powders can be compacted with ease. The sols have a relatively good binding ability since the compacted sol-coated powders can resist a rapid temperature change of up to 20 °C/minute. The comparative results for the compacted green pellets are shown in Figure 2.

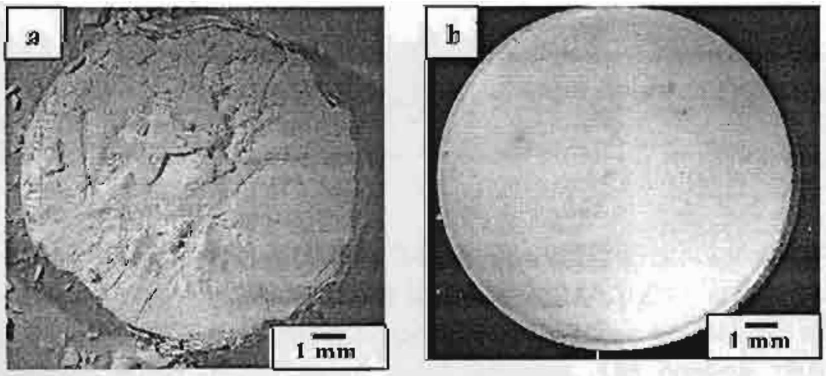

Figure 2: Comparative pictures of pressed specimens of (a) as-received powder and (b) the same powder but coated with magnesia sol

Thermograms for the yttria and magnesia dried gels are shown in Figure 3. The weight loss for yttria sol, occurs in three steps. The first step is the loss of adsorbed water. The second and third weight loss steps which occur in succession, starting from 300 °C, rising to 700 °C.

The SDTA result shows that the change of energy of this process is rather complicated, as indicated by the broadening and overlapping of the peaks but with a relatively small signals suggesting that these processes involve with small energy change . The thermal decomposition of the dried magnesia gel occurs in two steps; at 250 °C and 380 °C. These two steps are interpreted to be the oxidation process of the carbonaceous compounds as indicated by exothermic processes and the need for an adequate oxygen supply. Thermal decomposition of this gel is relatively much simpler than that of yttria gel.

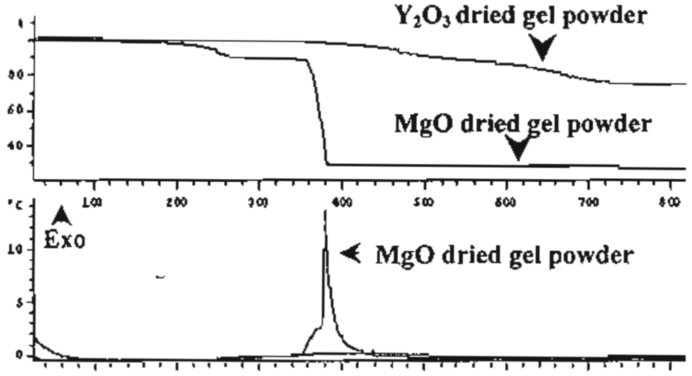

Figure 3: (above) TGA for the dried gels of yttria and magnesia sols and (below) corresponding SDTA curves.

The $MgO-ZrO_2$ specimen fired at 1600 °C for 8 hours mainly contains the monoclinic phase with a noticeable amount of cubic phase while the $Y_2O_3-ZrO_2$ specimen fired at the same condition shows three different phases, cubic tetragonal and monoclinic in which the monoclinic phase is only a trace (Figure 4). However, when the firing temperature is decreased to 1200 °C, proportions of the three phases only changes a little. The cubic/tetragonal phases starts to appear when the coated powders are fired at 1000 °C, indicating that a drastic diffusion of yttria into zirconia has occurred in this temperature region.

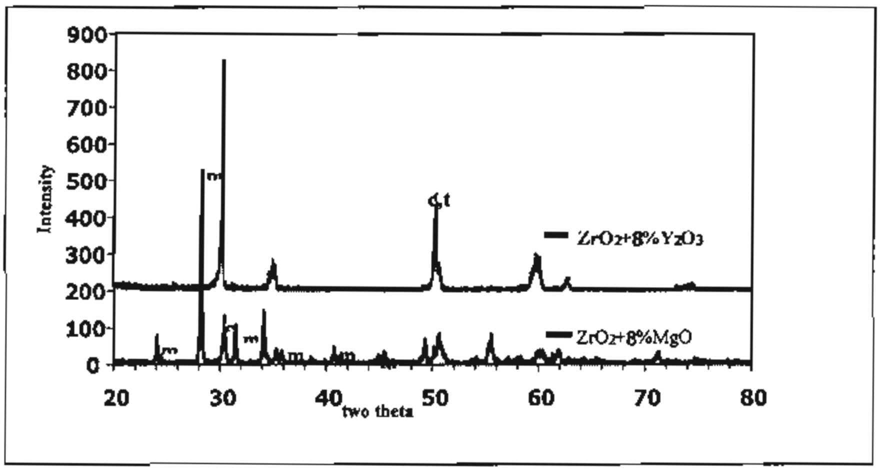

Figure 4: XRD patterns for sintered specimens of
(a) $Mg-ZrO_2$ and
(b) (b) $Y_2O_3-ZrO_2$.
(m :monoclinic,
t: tetragonal, c; cubic)

Figure 5 shows the SEM pictures of the MgO- and $Y_2O_3-ZrO_2$ specimens, both of which are fired at 1600 °C for 8 hours. The $MgO-ZrO_2$ specimen has a phase separation of two morphology grains. From the phase diagram of the $MgO-ZrO_2$ system, at 1600 °C, the material contains cubic + tetragonal solid solution. On cooling down to room temperature, the tetragonal has changed into monoclinic and exhibits a feathery structure while the cubic remains in the same structure. The $Y_2O_3-ZrO_2$ specimen, in contrast, shows a bi-modal structure of stabilized phase of cubic and tetragonal grains.

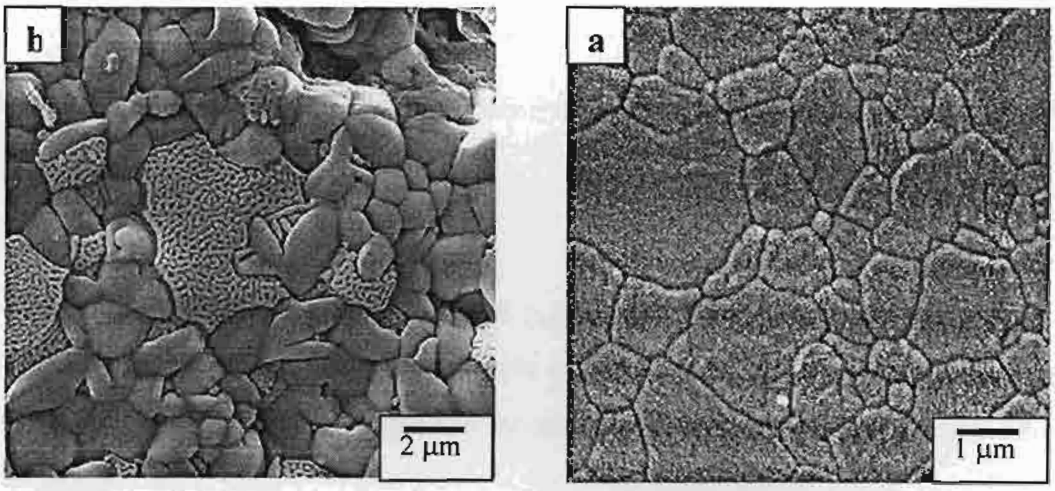

Figure 5: SEM micrographs for the sintered specimens of (a) Mg-ZrO_2 and (b) Y_2O_3-ZrO_2. Specimens were sintered at 1600 °C for 8 hours.

4. Conclusion

The coating sols which were also used in place of a conventional ceramic binder shows a relatively good binding ability. Diffusion of the Y_2O_3 diol sol into the zirconia powder has been shown to occur below 1000 °C, suggesting that stabilisation of zirconia in the high temperature structures has occurred at this temperature. Due to the phase separation and high content of the monoclinic phase in Mg-ZrO_2 specimens, higher sintering temperature and a more proper heat treatment schedule is required. However, this sol-powder technique is a potential technique for ceramic processing which a concentration gradient of a dopant may be required.

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A Novel Technique for Fabrication of Yttria Stabilised Zirconia

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Abstract

Yttria stabilized zirconia has been prepared using a simple sol-powder coating technique. The polymeric yttria sol which was prepared using 1,3 propanediol as a network modifier, was homogeneously mixed with nanocrystalline zirconia powder and it showed a dual function; as a binder which promoted densification and a phase modifier which stabilized zirconia in the tetragonal and cubic phases. Thermal analysis and X-ray diffraction revealed that the polymeric yttria sol which decomposed at low temperature into yttrium oxide could changed the m→t phase transformation behaviour of the zirconia powder probably by diffusion into the host zirconia powder at the temperature below 1000 °C probably due to the very high surface area of both yttria and zirconia particles. The sintered samples exhibited three crystalline phases, monoclinic, tetragonal and cubic in which cubic and tetragonal are the majour phases. The weight fractions of the individual phases present in the selected specimens were determined using quantitative Rietveld analysis.

Introduction

A wide range of potential applications exist for zirconia (ZrO_2) due to its advantageous properties, both mechanical or electrical, and this has stimulated extensive research over the past quarter century. When stabilized in the tetragonal phase (as tetragonal zirconia polycrystal-TZP), the product offers superior strength, toughness, and wear resistance, and thus can be used in applications such as a pump seals and components, cutting tools, abrasion wheels or as cutting instruments such a scissors. The polycrystalline oxide is ionically conductive above 600 °C, and in the cubic form is widely used as an oxygen sensor and as a component in the high temperature fuel cell. It is viewed as a key material for present and future energy applications, in its use as a solid electrolyte in fuel cell applications usually in the range 900-1000 ^{O}C.

Pure zirconia undergoes a phase transformation process on cooling below 1270°C from tetragonal-*(t)* to monoclinic-*(m)*, the main changes taking place over the temperature range 750°C to 970°C, depending on microstructure and composition. This process is accompanied, unusually, by a significant volume expansion and this often results in extensive cracking in the material, thus making the bulk use of pure zirconia impossible. To avoid this problem, dopants such as MgO or Y_2O_3 are added to stabilise or to meta-stabilise polycrystalline zirconia in either its high temperature cubic or tetragonal phase when cooled to room temperature.

Preparation of stabilized (cubic) zirconia powder can be achieved by several techniques such as plasma synthesis, co-precipitation, hydrothermal precipitation and sol-gel processing **[1-4]**. However, these techniques may well possess disadvantages such as compositional inhomogeneity in powder products, a requirement for complicated equipment, or difficult experimental procedures.

In this research, the authors propose a new technique for preparation of yttria doped zirconia by sol-powder coating. The polymeric yttria sol was synthesised using 1-3 **propanediol** as a network modifier and then mixed with the host zirconia powder. The polymeric yttria sol was added to the zirconia powder, not only did it act as a polymeric binder but also transformed into a fine powder at low temperature and helped fill intergranular spaces. This promoted densification and also stabilisation of the desired structure at room temperature by incorporation of the stabiliser into solid solution in the zirconia.

Experiments

1. Zirconia Powder

The zirconium oxide powder used in this research was donated by MEL Chemicals, Swinton, Manchester, England and was coded as SC101 by the supplier. (Zirconia (ZrO_2)+ Hafnia (HfO_2) was about 99 wt% in which Hafnia accounted for 2% of the total). The as-received powder was identified, using XRD, to be in the monoclinic form and had an average grain size reported in the material data sheet of 0.8 μm. However, this reported particle size was actually the size of the agglomerates of powder which could not be broken down during the particle size measurement. The particle size calculated using the equation :

$$D = 6/\rho As$$

is equal to 0.05 μm. A micrograph of the as-received powder is shown in Figure 9(a) and it reveals a raspberry morphology to the fine structure, a consequence of the precipitation of the precursor.

2. Polymeric Y_2O_3 sol synthesis

The Y_2O_3 sol was prepared as follows; firstly, yttrium nitrate hexahydrate [($Y(NO_3)_3.6H_2O$), 99.9%] (Aldrich) was mixed with 2,4 pentanedione [$CH_3COCH_2COCH_3$, 99+%] (Aldrich) in the molar ratio of 1 to 3. The mixture was kept under reflux at atmospheric conditions for 2 hours, when a clear-dark brown solution was obtained. When cooled, a 1 to 1 molar ratio of 1,3 propanediol [$HO(CH_2)_3OH$, 98%] (Aldrich) and yttrium was added to the mixture and kept under reflux for another 2 hours. The resulting sol was clear and again dark brown in colour. This sol was stable for over a year without precipitation or phase separation. The schematic diagram for the sol synthesis is shown in Figure 1. The yttria gel when fired at 700 °C has changed into yttrium oxide and has a very high specific surface area, as observed under SEM in Figure 9(b).

3. Preparation of stabilised zirconia and characterisation

A calculated quantity of Y_2O_3 sol (nominal composition of 8 %) was added to the ZrO_2 powder. Isopropanol was then added to the sol-powder mixture to make a homogeneous slurry which was kept under a stirring condition at 100 °C until the completely dried sol-coated-powder was obtained. The resulting powder was then sieved through a 120 nylon mesh and uniaxially pressed at 50 MPa to make cylindrical discs. Specimens were fired at 1400 °C, 1500 °C and 1600 °C for 1, 4 and 8 hours in a muffle furnace. The selected ramp rate was at 120 °C/hour from room temperature to 1200 °C. The samples were held at this temperature for 2 hours before being heated to the final temperature with a heating rate of 200 °C/hr. The cooling rate was set at 300 °C/hr. A schematic diagram for this process is shown in Figure 2. Phase identification was performed using powder XRD on selected samples, (D8 Advance, Bruker Germany). Samples were scanned through an angle from 20° to 80°, 2θ using step scan, with a 2θ sampling interval of 0.01°. Quantitative analysis of selected samples was performed using Rietveld analysis by DIFFRAC^{Plus} TOPAS software. Microstructural investigation was performed using SEM (LEO 1450VP). Thermal analysis, which was performed in a synthetic air atmosphere for the ZrO_2 powder, but in an oxygen atmosphere for the dried Y_2O_3 gel powder, was achieved using a TGA/SDTA 851^e STAR^e thermobalance (Mettler Toledo, Switzerland).

Results and Discussion

Thermal analysis

Figure 3, 4 and 5 represent the thermal analysis results of the as-received ZrO_2 powder, polymeric dried Y_2O_3 gel, and the Y_2O_3 sol-coated-ZrO_2 powder respectively. The TGA result for the loose ZrO_2 powder shows little weight loss from room temperature to ~ 200 °C. The loss of sample weight during this step is found to be an endothermic process and is most likely due to the loss of physically adsorbed moisture on the surface of the oxide powder. However, the sample did not show any further weight loss, as confirmed by its DTG curve. It is worth noting that the DTA curve still shows subsequent endothermic peaks. The first peak which is rather small, starts from 1130 °C to about 1173 °C. From the literature, the m→t transformation temperature has been reported to occur at about 1150°C-1170°C [5,6]. It is therefore possible that this endothermic peak corresponds to the latent heat of the solid-solid transformation process, as evidenced by the peak position and the enthalpy involved. The final endothermic peak is observed at about 1387 °C. From the literature, the transformation from tetragonal to cubic phase in pure zirconia should be at ~2370 °C [5]. Thus the presence of this endothermic peak should be attributed to another mechanism. However, this endothermic peak had disappeared when the same powder was reheated to 1600 °C. Only the m→t transformation endothermic peak is still observed in the latter case. Thus the emergence of this endothermic peak would most likely to be due to the degradation or decomposition of an impurity such as remnant sulfate salt which is reported by the supplier to exist in the form of SO_3 about 0.05 wt% in total. Since this amount is very small, the loss of sample weight is not measured with any certainty. (The decomposition temperatures for sulphates is generally about 800^{O}C, for $Zr(SO_4)_2$ the decomposition temperature is 410^{O}C (Rubber bible), so the peak is not due to that. It is more likely due to strain energy release on recrystallisation or grain growth, which can of course only happen once). Red → my comments

The polymeric dried Y_2O_3 gel loses about 26% of its total weight on heating to 1000 °C, as shown in Figure 4. The weight loss, as confirmed by its first derivative curve and DTA occurs in three steps. The first step, observed in the DTA diagram as a broad endothermic hump could be the loss of adsorbed water or the volatile solvent in the gel structure. However, this gel had been dried in an oven preset at 100 °C overnight and kept in a desiccator prior to measurement, so the volatile solvent should not be left over. This loss of sample weight is rather small, as is indicated by the small peak in the DTG curve. The emergence of this endothermic peak is thus believed to be due to the loss of adsorbed water, which may occur after drying process. The second and third weight loss steps of the dried Y_2O_3 gel occur in succession, starting from 300 °C, rising to 800 °C. These two steps are interpreted to be the oxidation process of the carbonaceous compounds as indicated by exothermic process and the need for an adequate oxygen supply. The DTA results show that this oxidation behaviour is rather complicated as indicated by the broadening and overlapping of the peaks.

Thermal decomposition of the Y_2O_3 sol-coated-ZrO_2 powder is considered to occur in a single step, starting at ~ 280 °C and ending at ~ 600 °C with a total weight loss of ~ 7% (Figure 5). This decomposition process is considered to be mainly due to the loss of the added Y_2O_3 sol. Where does the Yttria so go, this needs an explanation ? However, it is noticeable that the decomposition of the Y_2O_3 gel, when added to the ZrO_2 powder ends the reaction at a much lower temperature (about 200°C lower) than that of the Y_2O_3 gel alone, with much simpler curves. It is also apparent that the endothermic peaks in the high temperature regions observed in the DTA curve due to the m→t transformation and sulfate decomposition of the as-received ZrO_2 powder are not present in this coated powder. Instead, an extremely broad endothermic area starting from ~ 650 °C is observed. The disappearance of the m→t transformation peak suggests that the diffusion of yttria into the zirconia had occurred sufficiently to cause stabilization at lower temperature. The diffusion process necessary for this phenomenon that occur a considerably lower temperature than has been reported previously might possibly be due to a surface diffusion mechanism enhanced by the very high surface area of the yttria and zirconia (see Figure 9). Additionally the particle size of the crystallites is very small with the maximum corresponding diffusion distance only half their maximum dimension.The XRD results which will be shown later confirms that diffusion of yttria into the zirconia crystal had occurred below 1000 °C.

Powder Compaction

The mixture of Y_2O_3 sol and the ZrO_2 powder with an addition of 2-propanol was relatively stable i.e. no precipitation or phase separation was observed during the mixing process. The zirconia powder used in this research could not be compacted on its own, whereas the sol-coated powder could be compacted with ease. The comparative results for the compacted green pellets is shown in Figure 6.

Phase Identification

Figure 7 shows the XRD patterns of the loose powder fired at 700 °C, 1000 °C, 1200 °C and 1400 °C. The powder fired at low temperature (600 °C, 700 °C) appears to contain only monoclinic phase. At 1000 °C, the major phase is monoclinic, but a small peak corresponding to $(100)_t$ can also be observed. In contrast, the dominant phases observed at 1200 °C and 1400°C are tetragonal and cubic with a trace of $\mathbf{(11\bar{1})}_m$ remaining at 28.3° 2θ. The position of $\mathbf{(11\bar{1})}_m$ peak is relatively closed to the observation made by Gupta et. al. [7] and Pan et. al. [8] who reported it to be at 28.3° 2θ. The transformation from the monoclinic phase of the original powder to the tetragonal/cubic phases of Y_2O_3 sol-coated-zirconia powder indicates that diffusion of the yttrium into the host zirconia powder had already started below 1000 °C.

The XRD diffraction patterns for the compacted samples fired at 1400-1600 °C for 4 h are shown in Figure 8. It is apparent that the dominant phases in these patterns are tetragonal/cubic while the presence of a minor amount of monoclinic phase can also be observed. In the sample fired at 1400 °C, the reflection corresponding to the $(11\bar{1})_m$ is shifted to about 29.2 °2θ which is closer to the position of $(100)_t$. The compacted sample fired at the same temperature but different soaking times (1 and 8 hours) gives a similar result. However, the shift of the $(11\bar{1})_m$ peak position is neither found in the compacted samples sintered at higher temperature (1500 °C and 1600°C) nor in the loose powder fired at the same condition (1400 °C for 1 hour). The shift in the peak position could be due to a uniform stress inside the specimen [9] or more likely the decrease in the lattice parameter due to the substitution of yttrium ions the zirconium ion sites. Further work is still needed to clarify this point.

Quantitative phase analysis for the samples sintered at 1600 °C for 1 hour and 1500 °C for 8 hours, using Rietveld analysis, are shown in Table 1. The analysis is based on comparison of the measured data with calculated data. This analysis revealed that the selected samples contained three phases, monoclinic, tetragonal and cubic. The fraction of cubic and tetragonal crystals is fairly similar, whereas the amount of monoclinic crystal is small.

Table 1: Rietveld Quantitative phase analysis for the selected samples. (in weight %)

Sintering Condition	Cubic	Tetragonal	Monoclinic
1500 °C/8 hours	48.9	49.7	1.4
1600 °C /1 hour	45.9	52.3	1.8

Microstructure

The SEM pictures for the as received zirconia powder and the calcined yttria gel are shown in Figure 9. The microstructures of sintered samples (1400-1600°C for 4 hours) are shown in Figure 10. The sample fired at 1400 °C exhibits small grains with the average grain size below 1 μm, while the samples fired at 1500 °C and 1600 °C demonstrate a bimodal structure of small and large grains. From the literature, when yttria was introduced in the form of yttrium nitrate as the penultimate step before calcinations, it only decomposed into yttrium oxide and deposited on the skin of the host powder at 1200 °C. Firing at 1600 °C for several hours must be done to obtain uniformly dispersed yttria stabilised zirconia **[5]**. Generally the cubic phase consists of larger grains whereas the tetragonal phase consists of much smaller grains **[10]**. Thus increasing the firing temperature might both assist grain growth and alter the proportions of cubic and tetragonal phase present. In general the samples are dense suggesting that the polymeric Y_2O_3 sol acts as an effective binder to promote densification in the compacted samples.

Conclusion

Yttria stabilised zirconia has been prepared using a sol-powder coating technique in which the Y_2O_3 sol was introduced into the zirconia powder by a simple mixing method in a beaker. The powder attenuation (what do you mean?) step was not required in this technique. Diffusion of the Y_2O_3 diol sol into the zirconia powder has been shown to occur below 1000 °C by means of thermal analysis and the X-ray diffraction data possibly due to coating ability of the yttria sol onto the zirconia powder.

Diffusion of the yttria ions into the primary zirconia crystals occurs in fired samples which exhibits 3 phases; monoclinic, tetragonal and cubic in which the tetragonal and cubic are the dominant phases at high firing temperature (1200 °C upward) but the monoclinic phase was dominant at low firing temperature (below 1000 °C). It has been demonstrated that the polymeric Y_2O_3 sol can be employed as a binder to promote compaction and act as a source of phase stabilizer.

Acknowledgement

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