# Preparation of alumina–high zirconia microcomposite by combined gel-precipitation

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## Abstract

Microcomposites of alumina and zirconia containing equal volume fractions of the two are prepared by a combined gel-precipitation route using aluminium chloride and zirconium oxychloride as precursors. Dried gel powders calcined between 375 and 800 °C show cubic phase as the only crystalline phase. Zirconia gets converted to tetragonal phase above 900 °C and is retained mostly in this form upto 1000 °C. At the higher temperatures, it converts to the monoclinic phase. Alumina starts to crystallize into δ-form at 900 °C and is converted to α-form at 1250 °C. Pressed pellets sintered at 1400 °C achieve densities close to theoretical in 4 h. Microstructures show evidence of segregation and coarsening in a composite matrix of alumina and zirconia mixed at a submicron level.

*Keywords:* Alumina–zirconia microcomposites; Gel-precipitation; Powder processing

## 1. Introduction

Alumina, with its high stiffness, provides a matrix amenable to toughening through transformation of a dispersion of zirconia particles having a suitable particle size distribution [1,2]. The extent of toughening is limited by the problems involved in the densification of alumina matrix without coarsening the zirconia particles. The tendency towards coarsening increases with increasing volume fraction of the zirconia phase. Since particle size distribution is a critical parameter for transformation toughening, the volume fraction of zirconia that can be usefully employed in the process is limited. Attempts have been made to increase the fraction of zirconia through gel processing route using expensive organometallic precursors [3,4]. This process has now been used to prepare microcomposites containing upto 50% zirconia [5,6]. There are, however, no reports on the retention of zirconia in tetragonal phase and its transformability during fracture in these investigations. A simple process combining gelation and precipitation has been used to prepare alumina [7], spinel [8] and other multicomponent ceramics [9]. In this process, the concentration of the starting solution is increased to such an extent that during gelation process, when the gel becomes fully viscous, a substantial fraction of the starting solute is still in solution, that is in the liquid phase permeating through the gel network. On drying, this solute precipitates out in the pores between the hydroxide particles of the gel network

and upon calcination, it is decomposed to form oxide. This concept of combining gelation and precipitation has been extended to binary and ternary systems. In these systems, the different cations may be partitioning differently between the hydroxide network and the liquid phase. This method has the advantages simplicity and of using low cost, inorganic precursors. Here, we present the results of our work on preparation of alumina–zirconia microcomposites, having nominally equal volume fractions of the two phases, using this method.

## 2. Experimental procedure

Analytical reagent grade aluminium chloride ($AlCl_3$) and zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$) were used as the starting materials. Solutions of $AlCl_3$ was prepared with a concentration of 0.5 mol/l. $ZrOCl_2$ was then dissolved in this in such a proportion that will yield a final mixture of alumina and zirconia having equal volume fractions. For this calculation, alumina is assumed to have a density of 3.98 gm/cm$^3$ and zirconia to have a density of 6.1 gm/cm$^3$. Ammonia solution was added drop by drop to the mixed chloride, oxychloride solution with simultaneous magnetic stirring. Addition of ammonia solution was continued upto the point where the gel thus formed became fully viscous and the stirrer was stopped due to its viscous resistance. A small portion of the gel was dried at 80 °C and the dried powder was then subjected to: (i) thermal analysis, conducted in air in Netzch STA 409 using alumina crucible at a heating rate of 10 °C/min, and (ii) X-ray diffraction analysis, on Philips X'Pert system using Copper Kα radiation. Thermal analysis was also carried out on dried gels prepared separately from individual solutions of $AlCl_3$ and $ZrOCl_2$, respectively, in a similar manner, for comparison. The remaining gel was divided into different portions and directly heated to different calcination temperatures between 375 and 1250 °C and held for different predetermined periods (9 h for calcination at 375 and 450 °C and 4 h for all higher temperatures). The phase compositions were analysed using X-ray diffractometer.

For the study of densification behaviour of calcined powders, pellets of 1.25 cm diameter were prepared by uniaxial pressing using 2 wt.% PVA as organic binder. The pellets were heated at a rate of 3 °C/min until 600 °C and held there for 30 min followed by heating at a rate of 6 °C/min to different sintering temperatures (1350, 1400 and 1450 °C) for holding periods of up to 240 min. The temperature was maintained within ± 2 °C of the set temperature and the samples were cooled naturally within the furnace. Bulk densities of the sintered pellets were determined by the liquid displacement method. Microstructure of the cut and polished surface was observed under a scanning electron microscope (JEOL TX 330).

## 3. Results and discussion

The X-ray diffraction pattern of the gel dried at 80 °C (Fig. 1) shows sharply defined peaks of ammonium chloride. There are no other peaks for any other phase in this diffraction pattern. In particular, there are no peaks for any compounds, including chlorides and hydroxides, of aluminium or zirconium. Since the gel is prepared from a mixed solution of aluminium chloride and zirconium oxychloride using ammonium hydroxide as the destabilising agent, the gel is expected to contain hydroxides of aluminium and zirconium as well as the unreacted chloride/oxychloride. The diffraction pattern indicates that all such compounds are present in an amorphous form. Exactly the same x-diffraction patterns were obtained for the dried gel powders prepared from individual solutions of aluminium chloride and zirconium oxychloride, respectively.

The Thermal analysis (DSC and TG curves) of the three dried gel powders are presented in Fig. 2. The similarity in the decomposition behaviour of the three gels is remarkable. In all the three cases, the weight loss occurs in three broad steps covering almost the same temperature ranges. The DSC curve also shows similar characteristics features, with minor changes. At low temperature, upto just above 100 °C, there is a gradual weight loss associated with loss of excess water in the gel. There is a corresponding endothermic feature on the DSC curves around 100 °C. The second stage of weight loss starts from about 200 °C and extends upto about 325 °C except in case of zirconium oxychloride gel where this stage is complete below 300 °C. This is the major weight loss step and shows a corresponding endothermic peak around 316
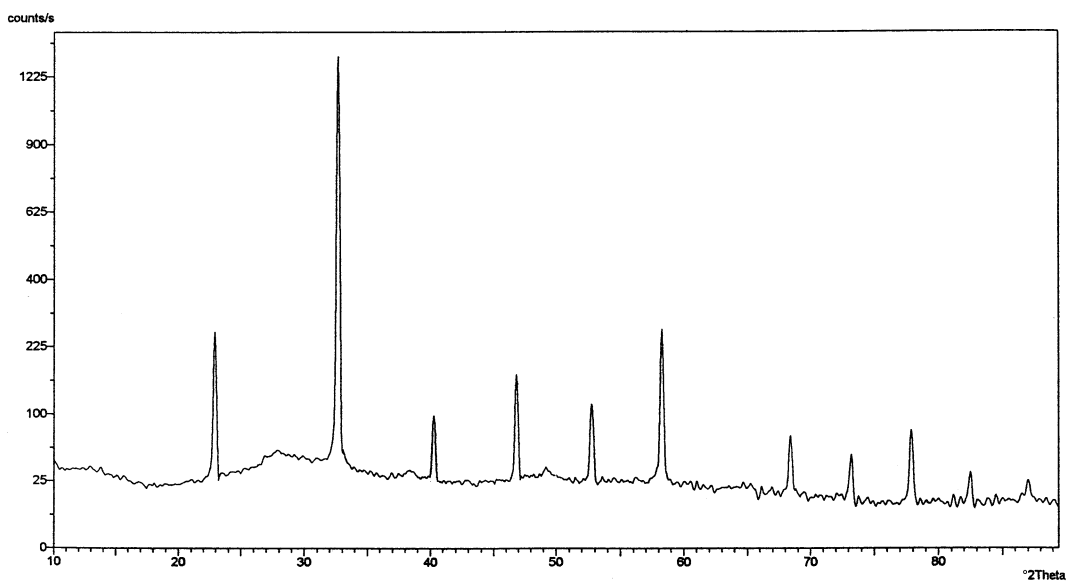
Fig.1. X-ray diffraction pattern of a dried powder

°C for AlCl$_3$ gel, 286 °C for ZrOCl$_2$ gel and 310 °C for mixed gel. This second stage is followed immediately by the third and last stage of weight loss that extends upto about 400 °C.

All the three gels show a well defined endothermic peak in the DSC curves at about 190 °C without a corresponding weight loss in the TG curves. This peak then indicates an endothermic reaction other than
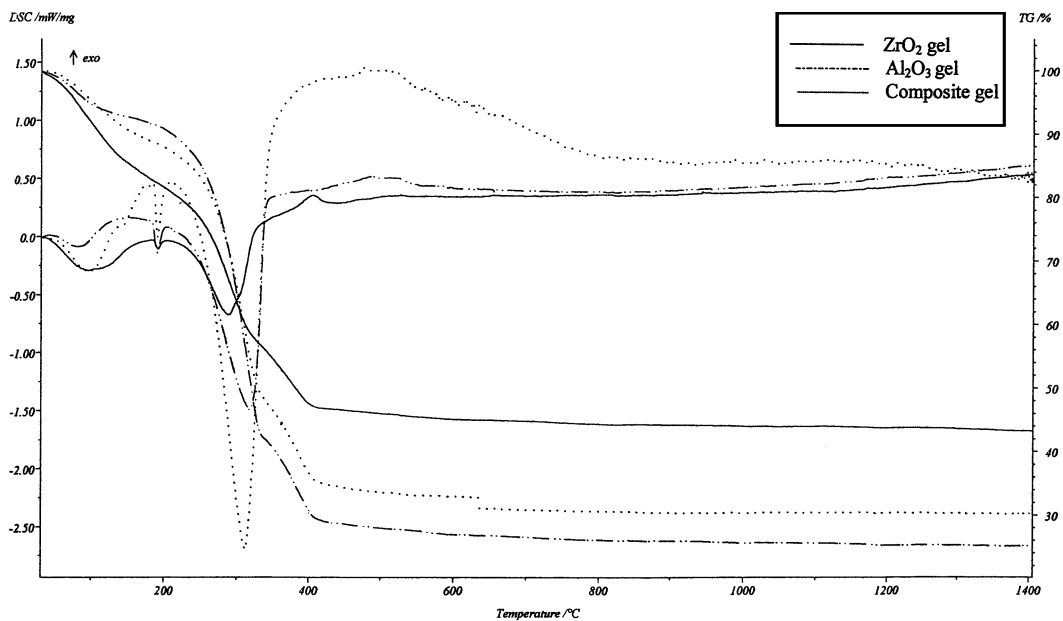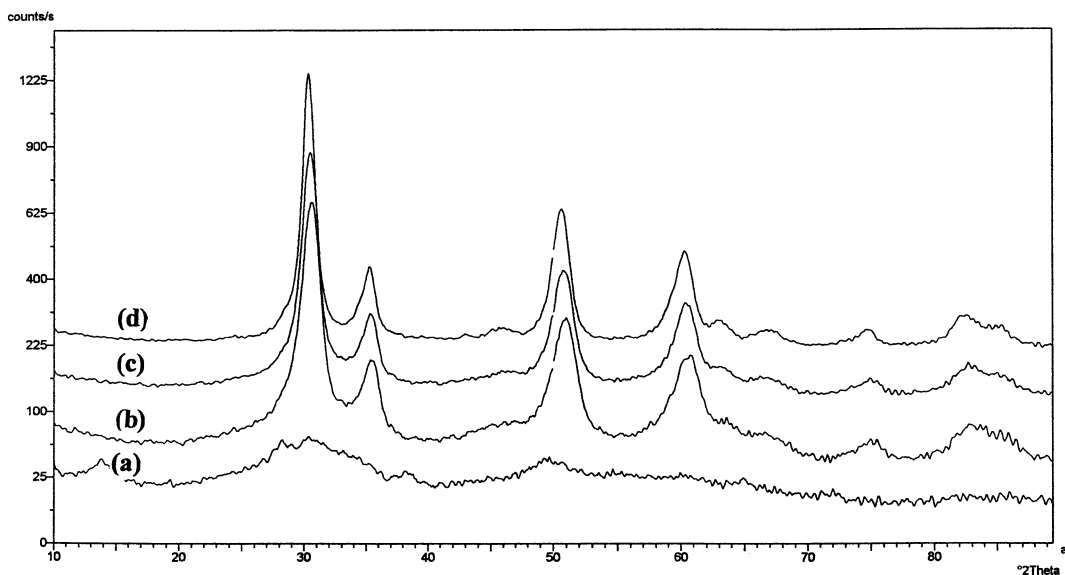


Fig. 2. DSC and TG plots of three dried gel powders: (———) ZrO$_2$ gel, (—·—) Al$_2$O$_3$ gel, (· · · · ·) composite gel.

decomposition. This reaction occurs both for aluminium chloride gel and the zirconium oxychloride gel and, hence, may be related to reaction involving ammonium chloride. The final decomposition step that is completed by about 400 °C in all the gels does not have a corresponding endothermic feature in any of the DSC curves. In case of aluminium chloride gel, the total weight loss in the final stage is about 52% of the weight of the material retained after completion of the decomposition (about 30% of the original weight). If the material retained is assumed to be alumina ($Al_2O_3$), the weight loss in this step is consistent with the decomposition of $Al(OH)_3$. This one-step decomposition behaviour, however, differs from the two step decomposition generally reported for $Al(OH)_3$. For the zirconium oxychloride gel, the weight loss in the last step is just under 30% of the weight retained (43%) after calcination. This corresponds to the decomposition of $Zr(OH)_4$. Similarly, for the mixed gel, the weight loss behaviour is consistent with the decomposition of mixed hydroxides of aluminum and zirconium giving nominally equal volume fractions of the two oxides.

The unusual aspect of this decomposition is, however, an absence of corresponding endothermic peak on the DSC curves. In the aluminium chloride gel, there is a broad exothermic peak around 485 °C due to the crystallization of some low temperature alumina phase while for zirconium chloride gel a better defined peak is observed for crystallization of zirconia just above 400 °C. In both cases, the exothermic trend starts well below the peak temperature. It may be concluded from this that the decomposition of hydroxide phases in these gels proceeds simultaneously with the crystallization of the resultant oxides and that the endothermic effect associated with the decomposition is masked by the exothermic crystallization. The DSC curve for the mixed gel does not have the peak for crystallization of zirconia. This may indicate suppression of crystallization of zirconia in presence of alumina (matrix constraint) or it may be the net effect of simultaneous decomposition of two hydroxides with crystallization of the two oxides.

Fig. 3 shows the X-ray diffraction pattern of the alumina−zirconia mixed gels calcined at different temperatures up to 800 °C. The gel sample calcined at 375 °C appears to have only two diffused peaks while those calcined at 450 °C and above, show well defined diffraction peaks. This is in agreement with the observation of zirconia crystallization peak around 400 °C in the DSC curve of the gel. The diffraction pattern matches with that of the cubic zirconia. (JCPDS File

to be fully tetragonal and hence it is slightly over-estimated. Even so, the density reaches close to the theoretical value in 4 h at 1400 °C. At 1350 °C, there is a very slow increase in density with time, from 92% of theoretical in 1 h to 93% in 4 h. At 1450 °C, the densities are only slightly higher, reaching a maximum of 94% in 2 h and then decreasing to 93% of theoretical in 4 h. This later high temperature trend is due to the influence of densification (pore removal) being offset by increasing transformation of zirconia to lower density monoclitic phase. The zirconia in retention tetragonal phase is 28% for pellets sintered

at 1350 °C for 1 h and reduces to 22% in 4 h. For pellets sintered at 1400 °C, tetragonal phase retention changes from 23% to 20% over the same holding period. For sintering at 1450 °C, retention is 16% and does not appear to change with time.

Scanning electron micrographs (Fig. 6a, b, c, d) show the microstructure on a cut and polished surface of the pellet at 1400 °C for 4 h. The lower magnification micrographs (Fig. 6a and b) show the structure in secondary electron mode (topographical contrast) and back scattered mode (phase contrast), respectively. The bright phase in back scattered mode is
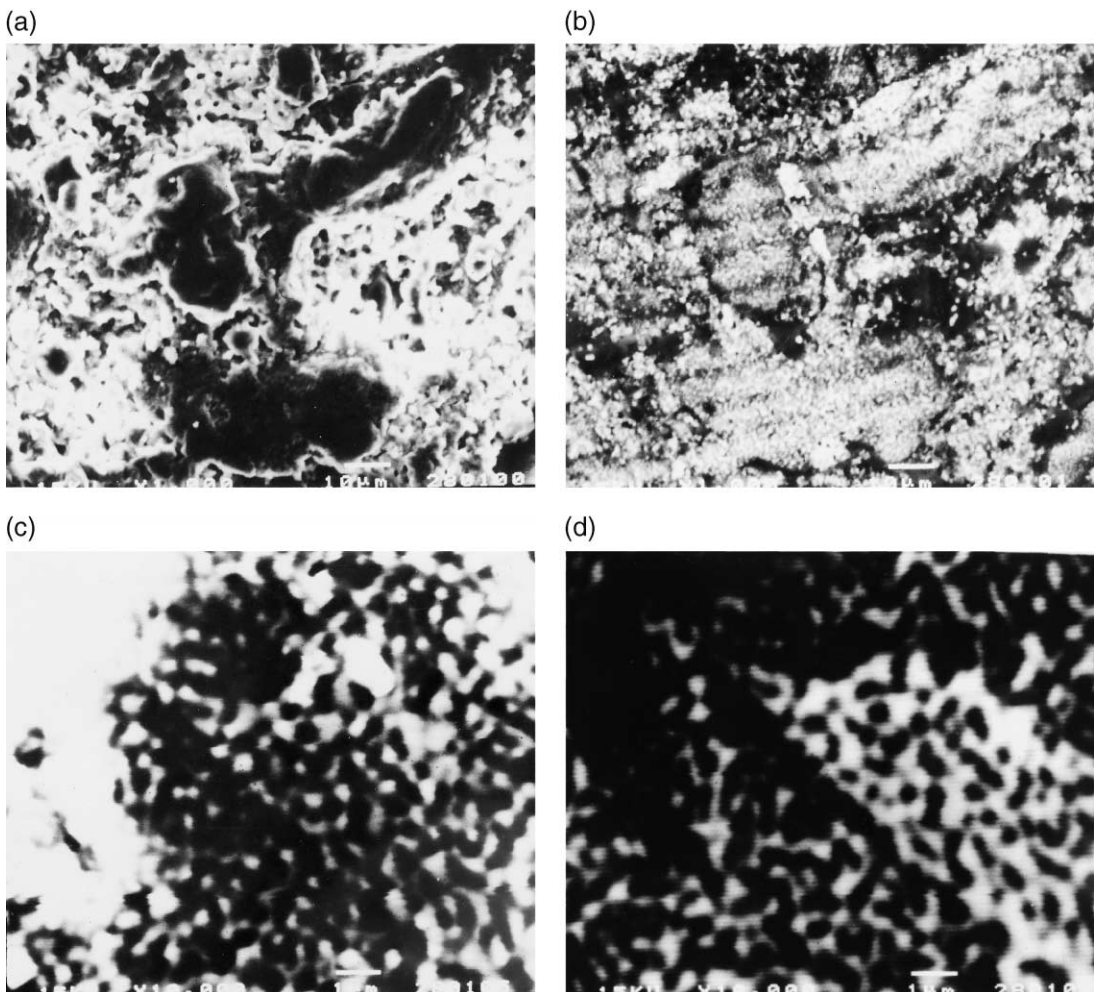
(a)

(b)

(c)

(d)



Fig. 6. Scanning electron micrographs of cut and polished samples at lower (a, b) and higher (c, d) magnification. (a) and (c) in secondary electron mode, (b) and (d) in back scattered electron mode.

no. 27-997). The tetragonal split is not observed in any of the peaks and there are no peaks for any phases of alumina. The peaks become sharper and shift slightly towards lower diffraction angles (higher *d* values) with increasing calcination temperatures.

Fig. 4 shows the diffraction pattern of the powders calcined at temperatures of 900, 1000 and 1250 °C, respectively. Zirconia is present in tetragonal and monoclonic forms in these sample. For calcination at 900 °C, 81% zirconia is present in tetragonal form whereas calcination at 1000 °C gives a tetragonal retention of 74%. However, the sample calcined at 1250 °C shows only 21% tetragonal retention. δ-phase of alumina appears on calcination at 900 °C and it is converted to α-alumina on calcination at 1250 °C.

It can, thus, be seen that zirconia crystallizes into the cubic form from the gel at a relatively low temperature and the cubic phase is stable even for calcination temperatures of upto 800 °C. Tetragonal form of is observed at 900 °C and largely retained upto 1000 °C. This may be a combined effect of fine particle size and the constraint placed by alumina. That no diffraction peaks of alumina are observe below calcination at 900 °C may be partly because of the low atomic scattering factor of aluminium and partly because of the poor crystallization of the phase.
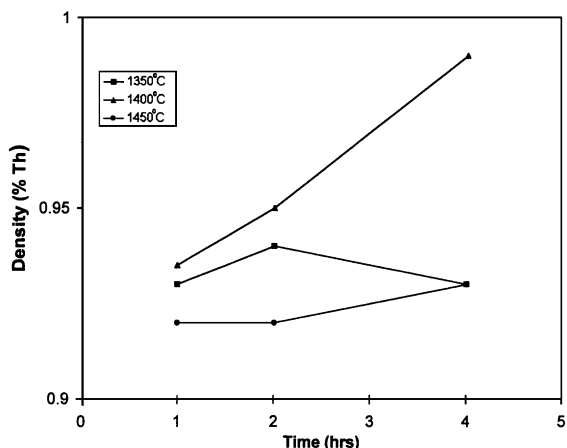


Fig. 5. Sintered density of pellets as a function of sintering time.

It, thus, appears that alumina and zirconia inhibit mutual crystallization and growth. Whatever be the degree of crystallization, the associated enthalpy appears to be sufficient to overwhelm the endothermic effect of dissociation of hydroxide phase.

The density (percentage of theoretical) of pellets sintered at 1350, 1400 and 1450 °C, respectively, as a function of sintering time, is plotted in Fig. 5. The theoretical density was calculated assuming zirconia
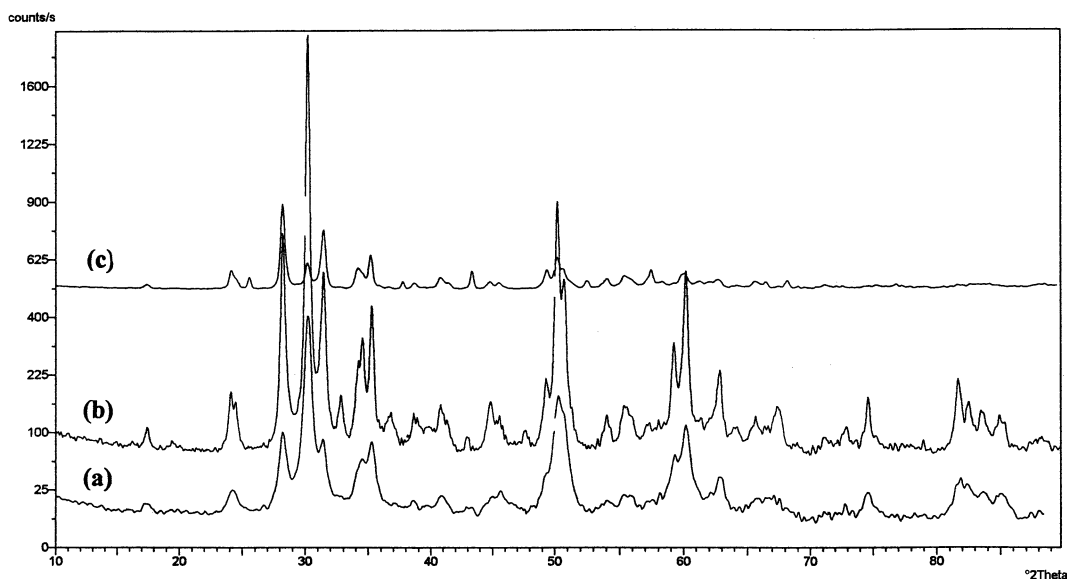


Fig. 4. X-ray diffraction pattern of alumina–zirconia mixed gel calcined at different temperatures: (a) 900, (b) 1000, (c) 1250 °C.

decomposition. This reaction occurs both for aluminium chloride gel and the zirconium oxychloride gel and, hence, may be related to reaction involving ammonium chloride. The final decomposition step that is completed by about 400 °C in all the gels does not have a corresponding endothermic feature in any of the DSC curves. In case of aluminium chloride gel, the total weight loss in the final stage is about 52% of the weight of the material retained after completion of the decomposition (about 30% of the original weight). If the material retained is assumed to be alumina ($Al_2O_3$), the weight loss in this step is consistent with the decomposition of $Al(OH)_3$. This one-step decomposition behaviour, however, differs from the two step decomposition generally reported for $Al(OH)_3$. For the zirconium oxychloride gel, the weight loss in the last step is just under 30% of the weight retained (43%) after calcination. This corresponds to the decomposition of $Zr(OH)_4$. Similarly, for the mixed gel, the weight loss behaviour is consistent with the decomposition of mixed hydroxides of aluminum and zirconium giving nominally equal volume fractions of the two oxides.

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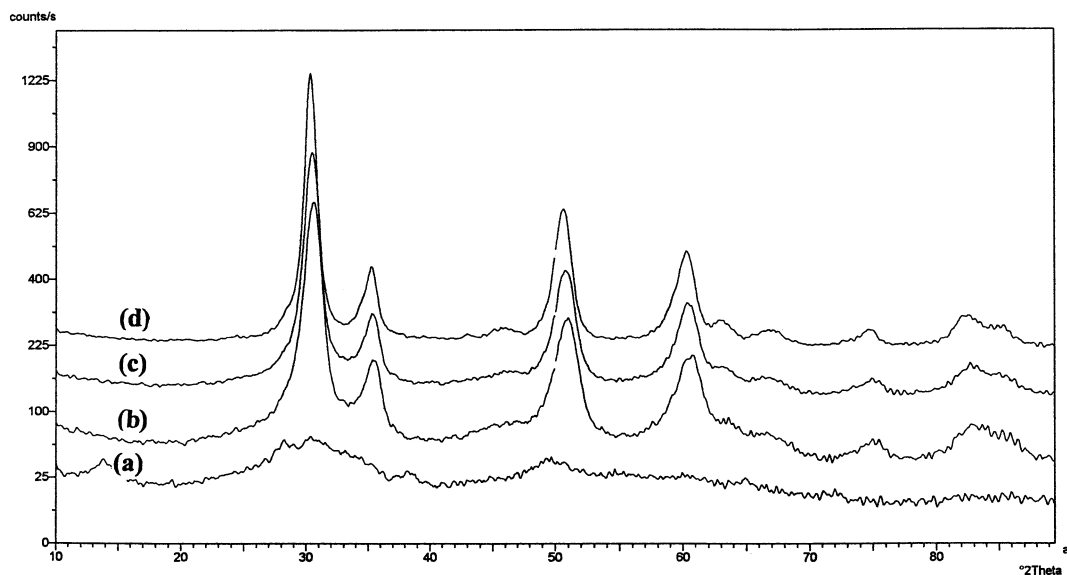


Fig. 3. X-ray diffraction pattern of alumina−zirconia mixed gel calcined at different temperatures: (a) 375, (b) 450, (c) 600, (d) 800 °C.