# Preparation of tetragonal zirconia powders by a solid state reaction: Kinetics, phases and morphology

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**Abstract.** Powders of tetragonal $(t)ZrO_2$ have been prepared by a solid state reaction between sodium metazirconate and sodium metaphosphate. The reaction temperatures and times have been varied between 450 and 550°C and 5 and 75 h, respectively. Zirconia powder, mostly in the $t$ and $t'$ phases, is obtained. The yield of $ZrO_2$ powder increases monotonically with time at all reaction temperatures according to a phase boundary controlled kinetics. The fraction of $t$ phase also increases with time at 450°C and 500°C but goes through a maximum at 550°C, the highest temperature employed. A maximum of 55% of the precursor monoclinic zirconia (used to prepare sodium meta zirconate) is converted to $t$ phase at 500°C/75 h. The $ZrO_2$ powder consists of crystallites of size 9–25 nm agglomerated into particles having average size between 2 and 4 $\mu$m. The agglomerates have a breaking strength of 100 MPa. A hydrothermal treatment is found to break the agglomerates into smaller sizes. Grinding the powder in a mortar and pestle converts only 12% of the $t$ phase into monoclinic, indicating that substantial fraction of the tetragonal phase is the non transformable variety $t'$. Heating experiments also confirm this.

**Keywords.** Tetragonal zirconia; powder preparation; solid state reaction.

## 1. Introduction

The tetragonal ($t$) to monoclinic ($m$) phase transformation of zirconia ($ZrO_2$), accompanied by 3–5% volume expansion and 8% shear strain, is utilized in toughening of ceramics. The stable phase of $ZrO_2$ at room temperature is monoclinic but the tetragonal phase can be stabilized if the particle size is very small or if $ZrO_2$ is alloyed with $Y_2O_3$, $CeO_2$ etc. Ultrafine $t$-$ZrO_2$ powders have been successfully prepared by a variety of methods (Mazdiyasni *et al* 1967; Haberko *et al* 1975; Brook 1980; Rhodes 1981; Kagawa *et al* 1983; Jean 1991; Mottet *et al* 1992; Suzuki *et al* 1992; Maher *et al* 1993). Harrison *et al* (1987) briefly reported some years ago a rather simple method for preparation of $t$-$ZrO_2$ powders having a crystallite size of $\approx 13$ nm by a solid state reaction between sodium metazirconate ($Na_2ZrO_3$) and sodium hexa metaphosphate ($NaPO_3)_6$ at relatively low temperature (500°C). The method converts coarse $m$-$ZrO_2$ to fine $t$-$ZrO_2$ in a two-step process: first the precursor $Na_2ZrO_3$ is prepared from coarse $m$-$ZrO_2$ and subsequently by a solid state reaction between $Na_2ZrO_3$ and $(NaPO_3)_6$, fine $t$-$ZrO_2$ powder is obtained. The $t$-$ZrO_2$ particles are observed to be agglomerated but are expected to break to finer particles during compaction. No further study on this preparation route has been reported.

This appeared to be an attractive process for preparation

of $t$-$ZrO_2$. We have therefore explored it further in this work, by conducting experiments under varying preparation conditions to optimize the yield of $t$-$ZrO_2$ powders. Objectives of this work were to study the kinetics of the solid state reaction and to ascertain the phases and preparation of the powder. Possibility of breaking the agglomerates by hydrothermal treatment and under compaction has also been studied. A key property of $t$-$ZrO_2$ is its ability to undergo $t \to m$ transformation in a stress field and the extent to which it is effective in enhancing toughness. An attempt has been made to evaluate these parameters also.

## 2. Experimental

The preparation method used here is essentially the same as described by Harrison *et al* (1987). A solid state reaction between $Na_2ZrO_3$ and $(NaPO_3)_6$ proceeds as follows

$$Na_2ZrO_3 + 1/6(NaPO_3)_6 \xrightarrow{500°C} ZrO_2 + Na_3PO_4. \quad (1)$$
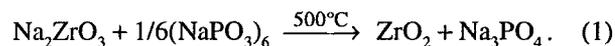
The precursor $Na_2ZrO_3$ for the above reaction was prepared by calcining a pellet of an equimolar mixture of $m$-$ZrO_2$ (1–2 $\mu$m size, Indian Rare Earths, Kerala) and $Na_2CO_3$ (Laboratory grade, Glaxo Laboratories, Bombay) at 1250°C for 90 min. The equimolar quantities of $Na_2ZrO_3$ and $(NaPO_3)_6$, (predried at 150°C) were

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mixed and ground in an agate mortar and pestle for 30 min and held in a Pt crucible at temperatures of 450°C, 500°C and 550°C for times ranging from 5 h to 75 h. $Na_3PO_4$ was removed from the reaction product by leaching with dilute $HNO_3$ (5 N) four times. The residue was washed with triple distilled water (4 to 5 times). Some unknown intermediate phase, besides zirconia, insoluble in $HNO_3$ was noticed, particularly in powders prepared at lower reaction times. This phase was removed by a further leaching with 1·5% HF solution for 10 min. The residual powders were again washed by triple distilled water followed by ethyl alcohol, dried at 60°C and weighed for determining yield of reaction. The phases present in the resulting $ZrO_2$ powder and their respective amounts were determined by X-ray diffraction (XRD) using a diffractometer (Reich Siefert 150 Debyeflex 2002) with CuK$\alpha$ radiation. The monoclinic volume fraction ($V_m$) was determined by the polymorph method as modified by Toraya *et al* (1984)

$$V_m = \frac{PX_m}{1 + (P - 1) X_m}.$$  (2)

where $P = 1\cdot31$, a constant factor to account for non-linearity and $X_m$ the integrated intensity ratio,

$$X_m = \frac{I_m(11\overline{1}) + I_m(111)}{I_m(11\overline{1}) + I_m(111) + I_t(111)},$$  (3)

$I(hkl)$ is the intensity of the ($hkl$) peak, given by the area under the respective ($hkl$) peak. The crystallite size ($D_{111}$) was determined by X-ray line broadening and the surface area of powders by single point BET method from which equivalent spherical diameter (esd $- D_{BET}$) was calculated. The morphology of powders was observed in a scanning electron microscope (JEOL, JSM 840A, Japan). It was noticed that the particles were agglomerated. The particle size was determined by Coulter Counter (Quantachrome, USA). The median particle size ($D_{50}$) corresponding to 50 wt% on the cumulative plot was used to calculate agglomeration parameter ($D_{50}/D_{BET}$). The nature of agglomeration of particles was studied by compaction of powders filled in a die (3 mm$\phi$) under pressure up to $\simeq$ 500 MPa, using a universal testing machine (Instron 1195). To study the possibility of breaking agglomerates to smaller aggregates by a hydrothermal treatment (HTT), the powder with calculated amount of water (to generate $\simeq$ 2 MPa steam pressure) was sealed in a quartz tube (8 mm outer diameter, wall thickness 1·5 mm) and held at 220°C for times up to 40 h. The resulting powder was again characterized with respect to crystallite size, surface area and particle size. To obtain an indication of the $t \rightarrow m$ transformability, the powder was ground vigorously in a mortar and pestle for 45 min. High temperature stability was determined by heating the powder at 1200°C and 1400°C. The

relative amounts of $m$ and $t$ phases were determined in each case.

## 3. Results and discussion

### 3.1 *Phases*

Figure 1 shows X-ray diffractogram from one of the powders. The predominant phase is tetragonal, though some monoclinic is also present. Sometimes it is hard to distinguish between the cubic and the tetragonal phases. However, in the present case the splitting of the (200)–(002) and (131)–(113) peaks, characteristic of the $t$ phase and absence of the 100% cubic peak at $2\theta = 30\cdot48°$ shows that it is the $t$ phase and not the cubic phase which is forming.

A $t'$ phase is also found to be present in the powders prepared at 450°C and 500°C (figure 2) but not in the powders prepared at 550°C. In $ZrO_2$ stabilized by alloying oxides such as $Y_2O_3$ etc, the $t'$ phase is considered to be a variant of the $t$ phase having a higher solute content which makes it less prone to stress induced $t \rightarrow m$ transformation. As shown later, the transformation of the powder on grinding or on heating is found to be difficult which is consistent with the presence of a $t'$ phase.

The stability of the tetragonal phase depends on the grain size, grain shape, stabilizer content and the constraint provided by the matrix. In the absence of a matrix constraint (e.g. for free powder) and with no stabilizer, the critical size for the $t$ phase to be stable is very low, $\simeq$ 30 nm. The average crystallite size of $ZrO_2$ prepared
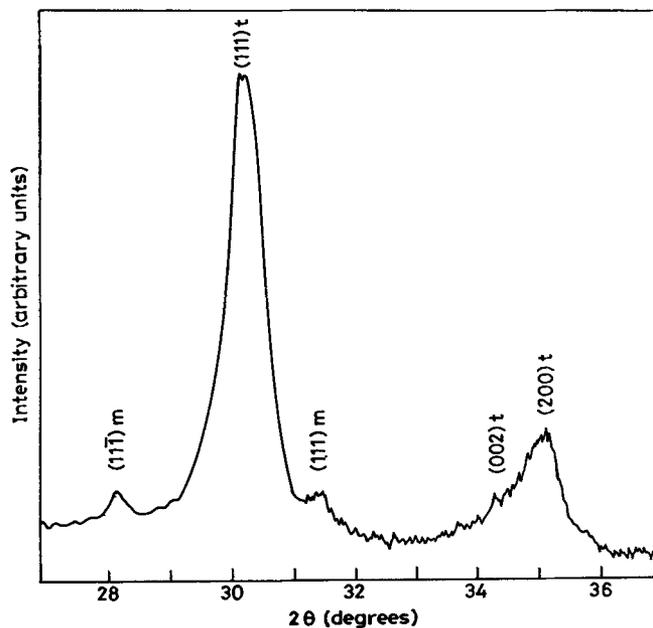


**Figure 1.** X-ray diffraction plot from $ZrO_2$ powder prepared at 500°C/75 h.

in the present experiment is well within this size as shown later. Hence stability of the $t$-$ZrO_2$ appears to be primarily due to the small crystallite size as also proposed by Harrison *et al* (1987).

As Na is present during the solid state reaction, it is possible that the $t$ phase may also be getting additionally stabilized due to oxygen vacancies and lattice strains created by dissolution of $Na_2O$ in $ZrO_2$. Benedetti *et al* (1989) have shown that 3 wt% Na stabilizes the cubic phase in $ZrO_2$. Nishizawa and coworkers (Nishizawa *et al* 1982, 1984) have also obtained similar results. In the powders prepared in the present work, the amount of Na in the $ZrO_2$ powders, as determined by atomic absorption spectrophotometer, was found to be too small (< 0·8 wt%) to stabilize the cubic phase. However, small amount of Na may contribute to the stability of the $t$ phase as reported by Sircar and Brett (1970) who found in their study of phase equilibria in the system $Na_2O - ZrO_2 - SiO_2$, the formation of $t$-$ZrO_2$ and attributed it to limited solution of $Na_2O$ in $ZrO_2$. The role of $Na_2O$ dissolved in $ZrO_2$ appears to be to increase the critical crystallite size up to which the $t$ phase is stable from $\simeq$ 30 nm for unalloyed $ZrO_2$ to $\simeq$ up to 50 nm as shown later in the SEM results (§ 3.3).

## 3.2 *Yield and reaction kinetics*

The yield ($\alpha$) of the process defined as the quantity of $ZrO_2$ obtained after the reaction as a fraction of the amount of $ZrO_2$ in the precursor (excluding unreacted monoclinic $ZrO_2$) is shown in figure 3. The yield increases with the reaction temperature. However the fraction of $(t + t')$ $ZrO_2$ in the total powder is maximum at an intermediate temperature as shown in figure 4. The optimum temperature appears to be 500°C where the yield is 67% out of which 84% is $(t + t')$ phase.
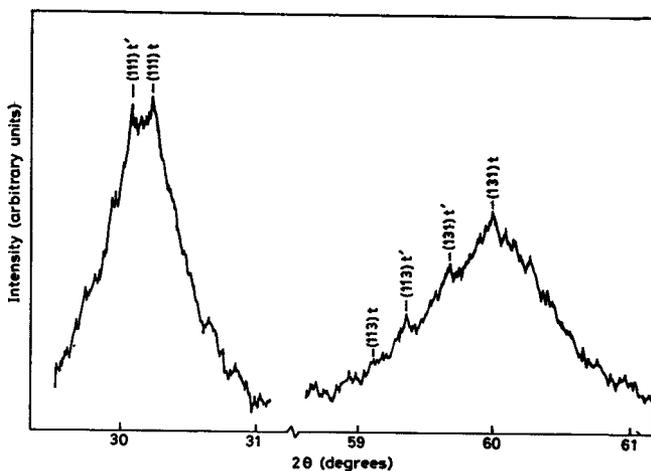
The yield data was analyzed using the general method for the treatment of isothermal solid state reaction as proposed by Hancock and Sharp (1972). The data fitted the following equation

$$1 - (1 - \alpha)^{1/3} = kt \quad \text{(phase boundary controlled-sphere)}, \tag{4}$$

with a high correlation coefficient (> 0·999 for 550°C) signifying that the reaction is most probably phase boundary controlled.

### 3.3 *Powder morphology*

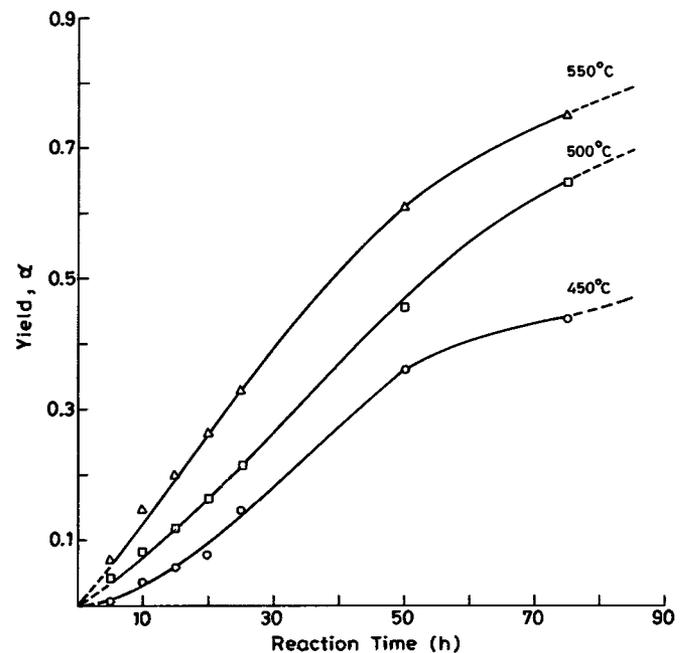The average crystallite size determined by X-ray line

**Figure 3.** Yield ($\alpha$) of $ZrO_2$ with reaction time at different temperatures.
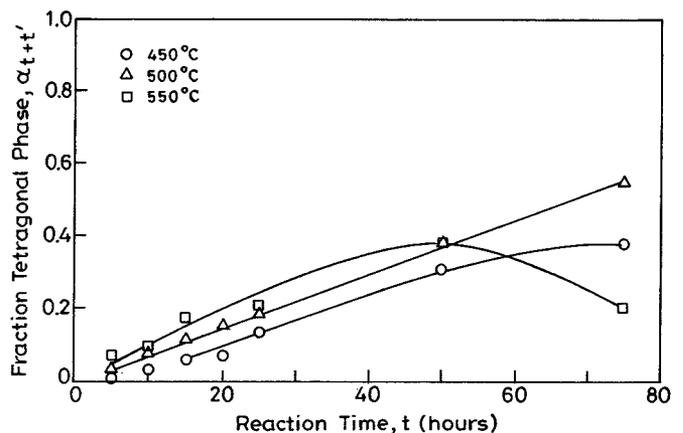
**Figure 4.** Yield of $(t + t')$ under different reaction conditions.

**Figure 2.** X-ray diffraction plots from sample prepared at 450°C/75 h showing the presence of $t'$ phase.

**Table 1.** Characteristics of the $ZrO_2$ powder obtained in the present experiments: properties of three powders from references is also given.

| Powder characteristics | This work Reaction time (75 h) | | | Roosen and Hausner | | Haberko and Pyda |
|---|---|---|---|---|---|---|
| | 450°C | 500°C | 550°C | Coprecipitated dried at 120°C | Coprecipitated freeze dried | Coprecipitated gels |
| Phase composition | 87% $t + m$ | 84% $t + m$ | 25% $t + m$ | Cubic | Cubic | Cubic |
| Specific surface area (m²/g) | 77 | 53 | 27 | 68 | 68 | 101·6 |
| BET particle size ($D_{BET}$ (nm)) | 12·9 | 18·9 | 37 | 16 | 16 | 10·5 |
| Crystallite size ($D_{111}$ (nm)) | 9 | 13·1 | 25·4 | 12·2 | 12·2 | 10·5 |
| Agglomerated particle median size ($D_{50}$ (μm)) | 2·1 | 2·05 | 4·3 | 1·9 | 0·7 | – |
| Agglomerate parameter ($D_{50}/D_{BET}$) | 162 | 108 | 116 | 127 | 44 | – |



**Figure 5.** SEM photograph of powders of $ZrO_2$ (500°C/75 h) showing agglomeration of particles.

broadening as well as by BET surface area and the particle size determined by a Coulter Counter are given in table 1. Data on some other powders reported in literature is also included. An SEM picture is shown in figure 5. It is seen that the powders consist of 10–50 nm sized crystallites agglomerated into particles of a few microns. The discrepancy in the X-ray and BET data is due to the assumption of a spherical crystallite in the latter and also due to the presence of contacts between the crystallites. The rate of increase in crystallite size during the reaction is nearly zero at 450°C (after the initial crystallites are formed, figure 6). At 550°C, the crystallite size increases with time at a nearly constant rate up to 50 h and then levels off. At 550°C, the behaviour is similar as that for 500°C up to 50 h but then there is a rapid increase in the average crystallite size. This appears to be due to the exaggerated grain growth which is found to occur during sintering of ceramics and is characterized by the growth of a few large grains to very large sizes at the expense of the smaller grains.

### 3.4 *Agglomerate strength by compaction test*

When an agglomerated powder is subjected to a uniaxial
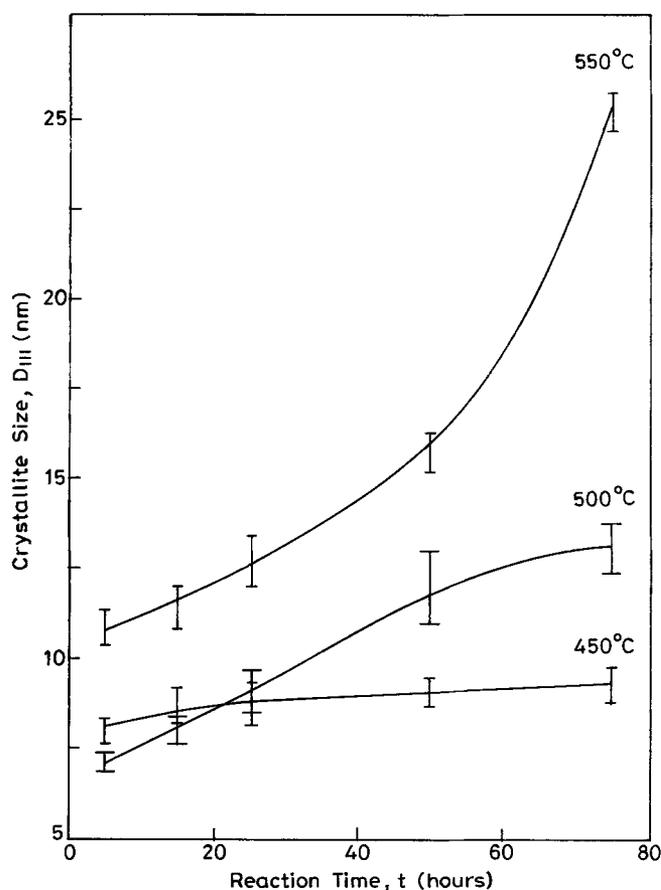


**Figure 6.** Crystallite size ($D_{111}$) of powders prepared at different times and temperatures.

pressure, the agglomerates break at a pressure indicated by a break in the plot of pressure vs packing density of the powder. Such a plot for 500°C/75 h powder is shown in figure 7. For comparison, data from literature (Graff *et al* 1980; Graff and Burggraff 1983; Haberko and Pyda 1983) for powders prepared by other methods is also included. It is seen that the powder prepared in
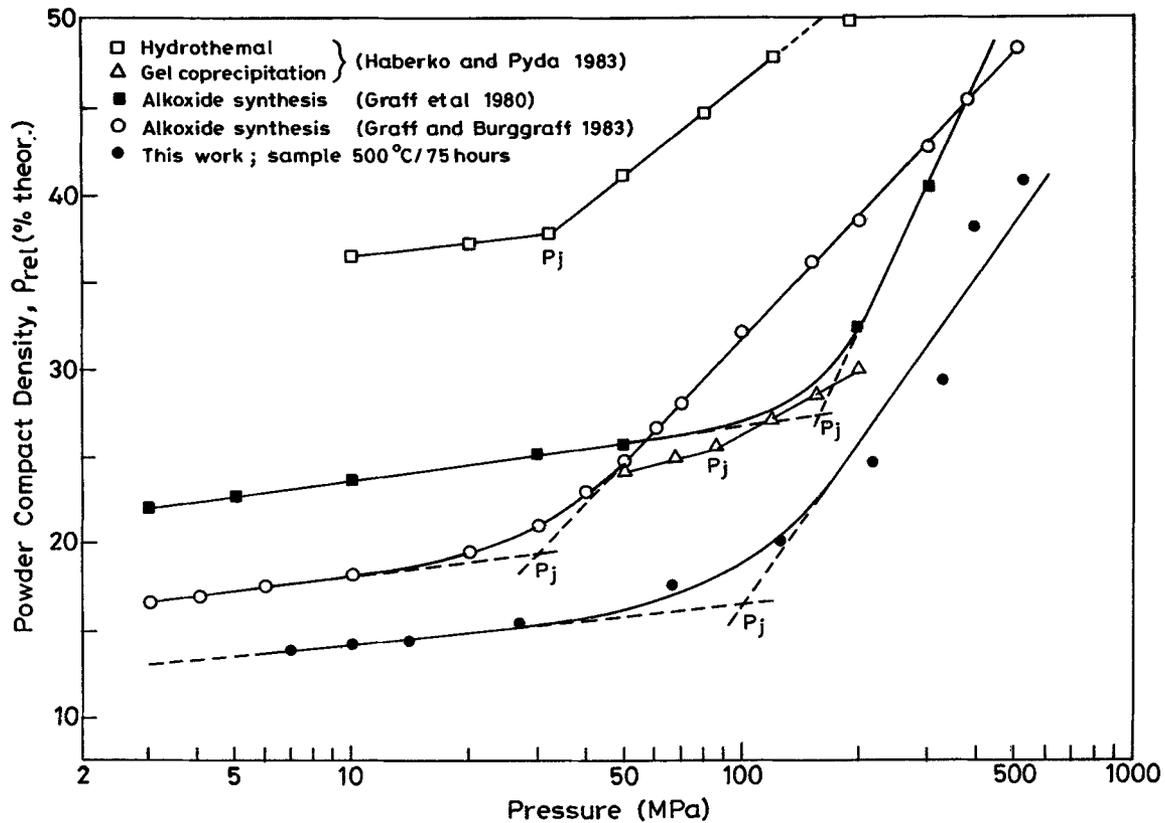
**Figure 7.** Powder compact density $\rho_{rel}$ vs compaction pressure, $P$, of the powder prepared at 500°C/75 h, compared to data reported in literature for powders by alkoxide synthesis, hydrothermal synthesis and coprecipitation/calcination methods.

**Table 2.** Effect of hydrothermal treatment on particle characteristics (500°C/75 h)

| | Surface area $(m^2g^{-1})$ | $D_{111}$ (nm) | $D_{BET}$ (nm) | $D_{50}$ coulter ($\mu$m) | $\dfrac{D_{50}}{D_{BET}}$ |
|---|---|---|---|---|---|
| Before HTT | 53·2 | 13·1 | 18·9 | 2·1 | 108 |
| After HTT (40 h) | 57·0 | 12·9 | 19·6 | 1·6 | 83 |

this work has a high agglomerate breaking strength (100 MPa) and a low packing density (Powder compact density $p_{rel} = 13\%$) at low pressure ($\simeq 3$ MPa). The latter result is due to the poor flow characteristics of the powder and may also be due to a low agglomerate density. The low agglomerate density implies that the crystallites maintain their individuality in the agglomerates to a large extent. This is supported by the earlier results that they are predominantly tetragonal and have high specific surface area. Thus these powders have strong solid bridges between crystallites and appear to be quite porous.

### 3.5 *Effect of hydrothermal treatment*

Hydrothermal treatment has been found to be quite

effective in breaking agglomerates in a $TiO_2$ powder by Heistand *et al* (1985). To study this effect the $ZrO_2$ powders obtained by reaction at 500°C/75 h were subjected to a hydrothermal treatment for 40 h in a quartz tube using 2 MPa steam at 220°C. The results are given in figure 8 and table 2. The hydrothermal treatment shifts the particle size distribution to lower sizes, with agglomerates larger than 6 $\mu$m totally eliminated. The average particle size comes down to 1·6 $\mu$m from 2 $\mu$m. There is no change in the crystallite size. However, the agglomerate parameter (agglomerate size/crystallite size) is reduced from 108 to 83 indicating that significant number of bonds between crystallites are broken under the conditions of hydrothermal treatment used. Further reduction in agglomerates may be produced by using higher pressures and temperatures during the hydrothermal treatment.

### 3.6 *Transformability under stress and on heating*

The powder (500°C/75 h) was crushed in mortar and pestle for 30 min. Only 12% of the $t$-$ZrO_2$ transformed to monoclinic indicating the presence of considerable amount of the $t'$ phase. The powder was heated to different temperatures, held for 1 h and cooled to room temperature to determine the extent of $t \rightarrow m$ transfor-
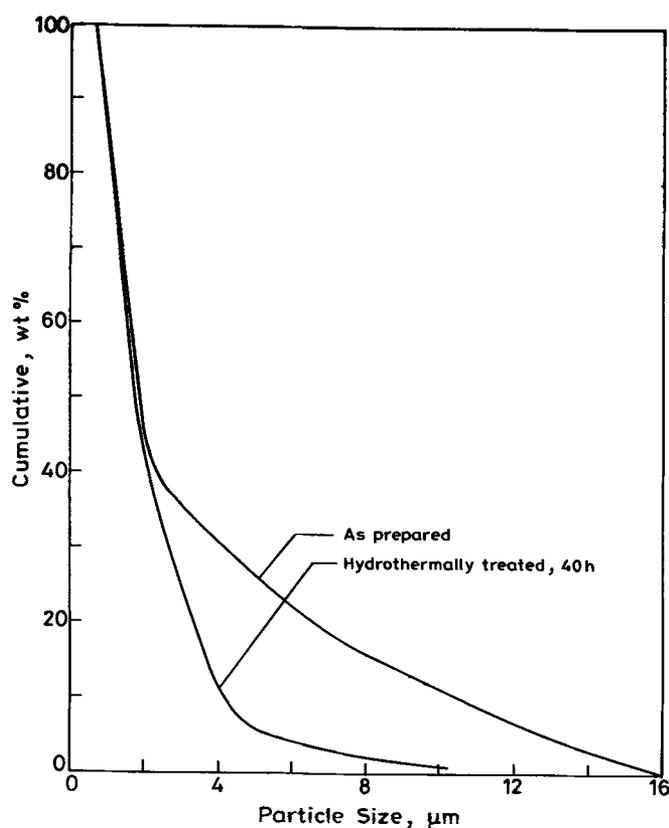
**Figure 8.** Particle size distribution of powder prepared at 500°C/15 h.

mation. Heating to 1200°C resulted in only slight increase in the monoclinic content while heating to 1400°C converted all the $(t + t')$ to monoclinic phase. Pellets sintered at 1550°C were also fully monoclinic. The $t'$ phase is stable up to 1400°C. Above experiments thus show that most of powder prepared at 500°C exists as $t'$.

### 4. Summary

The solid state reaction used in the present work is successful in producing tetragonal zirconia. The kinetics of the reaction appears to be phase boundary controlled. The yield of tetragonal $ZrO_2$ is found to be maximum at 500°C where 84% of the powder is in the $t$ phase. The zirconia crystallites, 9–25 nm in size, are agglomerated into particles of 2–4 $\mu$m. A substantial fraction of the powder is found to be in a nontransformable $t'$ form. The factors which lead to this need to be understood in order to make these powders useful for toughening applications. The agglomerates have a breaking strength of 100 MPa which is well within the pressures used during dry pressing of ceramics. In order to exploit the property of the stress induced $t \rightarrow m$ transformation in $t$ zirconia, it may be necessary to

incorporate some stabilizer (e.g. $Y_2O_3$, $CeO_2$) in the powder and also to reduce the agglomerate size. A hydrothermal treatment is found to be useful in reducing the particle size substantially.

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