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X-ray Diffraction Study of Phase Transformation in Hydrolyzed Zirconia Nanoparticles

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Abstract

The occurrence of metastable tetragonal (t′) phase and its transformation into monoclinic (m) in nanocrystalline ZrO₂ were systematically studied by using X-ray diffraction with respect to the grain size and processing conditions. The zirconia particles in the average size range 7–20 nm were prepared by hydrolyzis of zirconium oxy-chloride solution for different hydrolyzing periods. Drastic changes in grain size and the phase formation with the hydrolyzing time were observed. The amorphous ZrO₂ crystallizes in the t′ phase around 718 to 753 K on heating. However, if the crystallization occurs during the hydrolyzis itself, the monoclinic phase is formed even the grain size is less than 10 nm. The microstructural defects seem to dominate the grain size effect causing the reduction in crystal symmetry in the nanocrystalline zirconia obtained after 72 h of hydrolyzis. © 1999 Elsevier Science Limited. All rights reserved

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1 Introduction

The structural and related physical properties of nanocrystalline materials have been the subject of materials science in recent years. Many experimental and theoretical investigations on the interfacial and surface structure of nanocrystalline materials have been made during the past decade.[1–3] But the effects from the internal microstructure of the nanograins and chemistry of the grain assemblages are still to be better studied and understood.

Zirconia (ZrO₂) is one of the technologically important and widely studied materials in the aspects of structural, mechanical and electrical properties. The ZrO₂ exists in three polymorphs: cubic (c), tetragonal (t) and monoclinic (m) at various temperature ranges.[4] The monoclinic phase is the thermodynamically stable phase at room temperature. However, by tailoring the processing conditions and microstructure, it is possible to obtain a metastable tetragonal (t′) phase of ZrO₂ at room temperature.[5] The tetragonal or cubic phase stabilization and the associated phase transformation processes seem to depend on the grain size to a certain extent and more dependent on the chemical composition of the powders.[6,7]

It has been observed that when amorphous ZrO₂ powder is heat treated, it first crystallizes in the metastable tetragonal phase and then transforms into the stable monoclinic phase on further heating.[8–11] The powders prepared by chemical methods usually show the above features. The purpose of the present investigation is to study the effect of hydrolyzing conditions during preparation and the microstructural effects of the grain assemblages on the phase transformations in the amorphous and crystalline ZrO₂ powders obtained by the precipitation technique. X-ray diffraction (XRD) and Differential thermal analysis (DTA) methods were employed, for structural characterization of these powders prepared under various thermal hydrolyzing conditions.

2 Experimental Details

The nanocrystalline ZrO₂ powder was prepared by the method of hydrolyzis: an aqueous solution

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(0·1 mol/1) of zirconium oxy-chloride (ZrOCl$_2$. 8H$_2$O) was taken in a flat bottom flask fitted with a reflux condenser.[12] The solution was hydrolyzed (boiling–evaporation–condensation) for different periods (e.g. 24, 48, 72 and 140 h) then neutralized and coagulated with ammonia solution. White precipitates were obtained and filtered. The particles were then washed, dried and ground for 5 min in an agate mortar.

The powder samples obtained after hydrolyzing the solution for 24, 48, 72 and 140 h are coded for convenience as Z24H, Z48H, Z72H and Z140H and the unhydrolyzed one as Z0H. The samples were heat treated at 673, 773, 923, 1073 and 1273 K for 1 h and subjected to X-ray diffraction using a Seifert high resolution diffractometer with CuK$_{\alpha 1}$ radiation and quartz monochromator. To check the role of oxygen stoichiometry in the $t'-m$ phase transformation in the unhydrolyzed zirconia sample, the powder was annealed in a vacuum of 5×10^{-6} torr in a quartz tube and XRD was carried out. A small amount of tetragonal phase was observed along with the predominant monoclinic phase. Thus the oxygen stoichiometry has also been found to have some effects on the phase transformation.[4] The average grain size of the ZrO$_2$ powders were determined by using the Scherrer formula from the width of the X-ray diffraction lines.[13] The quantitative determination of the volume fraction of t' phase ($X_{t'}$) in the mixture of both monoclinic and tetragonal phases was made by using the formula[14]

$$x_{t'} = \frac{I(111)_{t'}}{I(\bar{1}11)_m + I(111)_m + I(111)_{t'}},$$

where the subscripts m and t' refer to the monoclinic and metastable tetragonal phases and I refers to the X-ray intensity of the corresponding peaks. Differential thermal analysis (DTA) experiments were carried out for all the samples by using a Perkin–Elmer DTA 1700 model in the temperature range from 333 to 1473 K with a heating rate of 10 K min^{-1}. The enthalpy of the crystallization process in Z0H and Z24H samples was determined from differential scanning calorimetry (DSC) experiments.

3 Results

The powder X-ray diffractograms of the as-prepared ZrO$_2$ samples obtained after different hydrolyzing times are shown in Fig. 1. The un-hydrolyzed and 24 h hydrolyzed samples (Z0H and Z24H) seem to be amorphous. The increasing intensity of the XRD peaks in the case of the samples hydrolyzed for more than 48 h indicate that the compound is
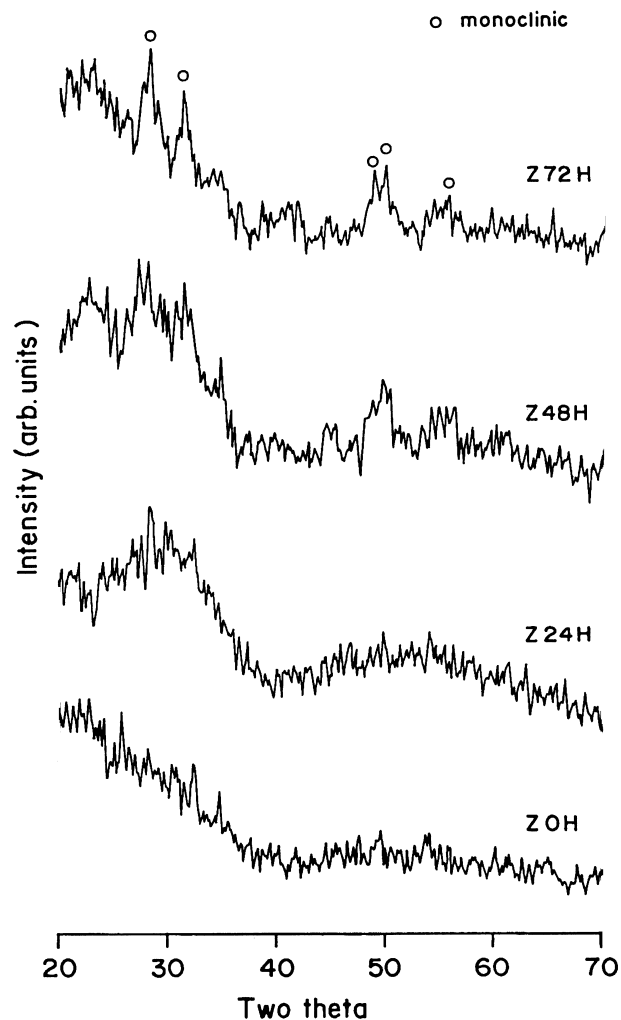

Fig. 1. XRD spectra of as-prepared ZrO$_2$ obtained after different hydrolyzing periods.

crystallized in the monoclinic phase during the process of hydrolyzis. Figure 2 shows the DTA thermograms of Z0H, Z24H, and Z48H powders. A broad endothermic peak at around 400 K for all the three samples and an exothermic reaction at 718 and 753 K for Z0H and Z24H samples, respectively, were observed.

Figure 3 shows the XRD spectra of the nanocrystalline ZrO$_2$ powders obtained after different hydrolyzing periods and annealed at 773 K for 1 h in air. The Z0H and Z24H samples exhibit predominant tetragonal phase. The Z48H sample exhibits a mixture of both tetragonal and monoclinic phases whereas the Z72H and Z140H samples show only monoclinic phase. It is observed that the diffracted X-ray intensity of the main peak (1 1 1) at $2\theta = 30\cdot1°$ of the t'-phase is quiet high in Z0H powder compared to the others (but in the figure, for convenience, all the spectra were drawn in an arbitrary intensity scale). The volume fractions of the metastable tetragonal phase, lattice parameters and the average grain size of the ZrO$_2$ powders obtained for different hydrolyzing times are given in Table 1.
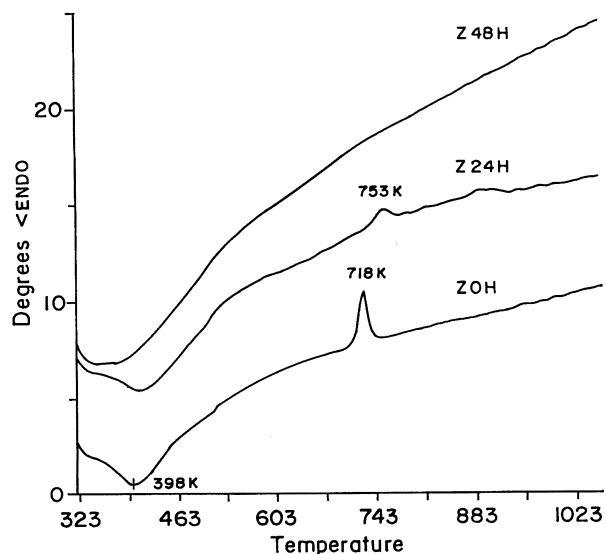
Fig. 2. Differential thermograms of as-prepared ZrO_2 powders.

The XRD spectra of Z0H samples annealed at different temperatures are shown in Fig. 4. The powder annealed at 773 K is predominantly in tetragonal phase as discussed earlier, and as the temperature is increased, the monoclinic phase is growing at the expense of the metastable tetragonal phase. Above 1073 K, the sample is totally of monoclinic phase. When the sample is annealed at 1273 K in vacuum, a small percentage of tetragonal phase is observed. Figure 5 shows the XRD spectra of the Z24H samples annealed at various temperatures. In this case, the peak (111) of the t'-phase is observed even for the sample annealed at 673 K. The metastable tetragonal phase is retained up to the annealing temperature 1073 K and transforms into the thermodynamically stable monoclinic phase for higher annealing temperatures. Only a little percentage of the t'-phase was observed in the powder annealed at 1273 K.

4 Discussion

4.1 Effects of hydrolyzing time

The X-ray diffraction analysis of the as-prepared and the annealed powders reveals that the phase stabilization process in the ZrO_2 has a dependence on the hydrolyzing time and annealing temperature. In the as-prepared form, the Z0H and Z24H powders are found to be amorphous and they crystallize to a metastable tetragonal phase on heating. The crystallization phenomenon is seen in the DTA thermogram (Fig. 2). In the DTA spectra, the endothermic reactions are attributed to the release of adsorbed water molecules and the exothermic ones are assigned to the crystallization of amorphous ZrO_2. The reason for the difference of 25 K in the crystallization temperature of the
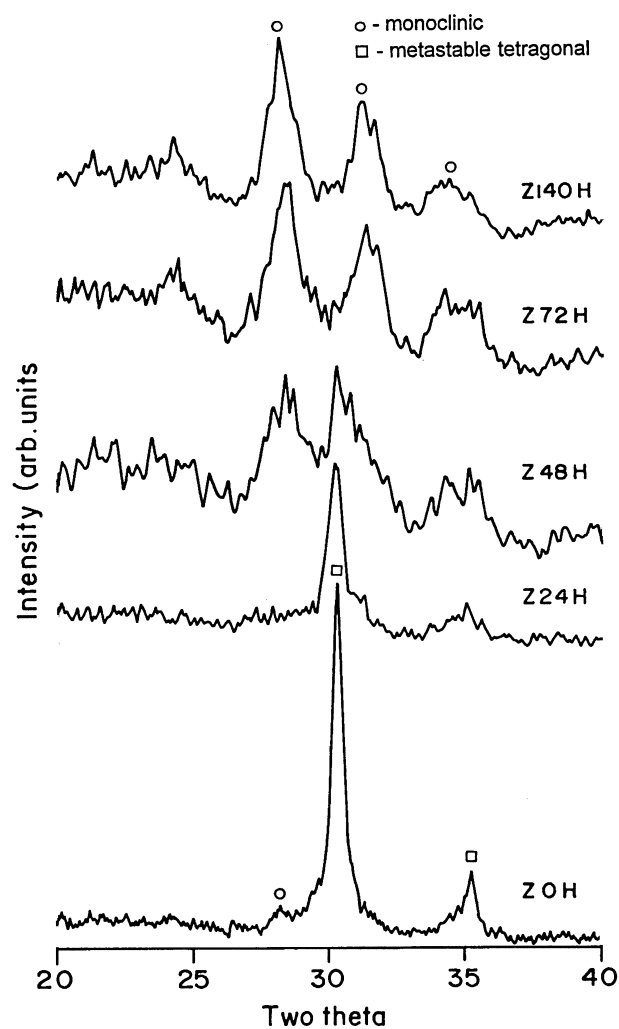

Fig. 3. XRD spectra of nanocrystalline ZrO_2 powders obtained after different hydrolyzing periods and annealed at 773 K for 1 h.

two samples is not clear. The enthalpy of the crystallization reactions estimated from DSC are found to be 2·37 and 1·85 kcal/mol for the Z0H and Z24H samples, respectively. The decrease in the crystallization enthalpy for higher hydrolyzing time can be attributed to the extent of crystallinity present in the sample. Whereas the Z48H, Z72H and Z140H powders are found to be crystalline, predominantly in the monoclinic phase, as evidenced by the XRD spectra of the as-prepared samples (Fig. 1) and the disappearance of the exothermic (crystallization) peak for the Z48H sample in Fig. 2. Thus, if the amorphous ZrO_2 powder undergoes a transition from amorphous to crystalline, it crystallizes in the metastable tetragonal phase, and if the crystallization occurs during the hydrolyzis process itself, only the monoclinic phase is stabilized. The variations in the c/a ratios of the metastable tetragonal phase and the deviations in the monoclinic lattice parameters from that of the crystallographic values ($a = 5·147$; Å, $b = 5·213$; Å, $c = 5·313$; Å and $\beta = 99·22°$)[15] as seen in Table 1

Table 1. Volume fractions of the metastable tetragonal (t') phase, grain size and lattice parameters of ZrO_2 powders obtained after different hydrolyzing times (the powders were annealed at 773 K for 1 h)

Sample code	Hydrolyzing time (h)	Vol. fraction of the t' phase (%)	Lattice parameters* Å	Grain size (nm)
Z0H	0	85	$a_{t'} = 5.113$, $c_{t'} = 5.187$ c/a 1.014	16
Z24H	24	73	$a_{t'} = 5.112$, $c_{t'} = 5.239$ c/a 1.025	12
Z48H	48	42	$a_{t'} = 5.110$, $c_{t'} = 5.21$ $c/a = 1.019$	17
Z72H	72	5	$a_m = 5.282$, $b_m = 5.232$ $c_m = 5.126$, $\beta = 97.79°$	8
Z140H	140	0	$a_m = 5.299$, $b_m = 5.235$ $c_m = 5.138$, $\beta = 98.730°$	9

*Subscripts t' and m stand for the metastable tetragonal and monoclinic phases, respectively.
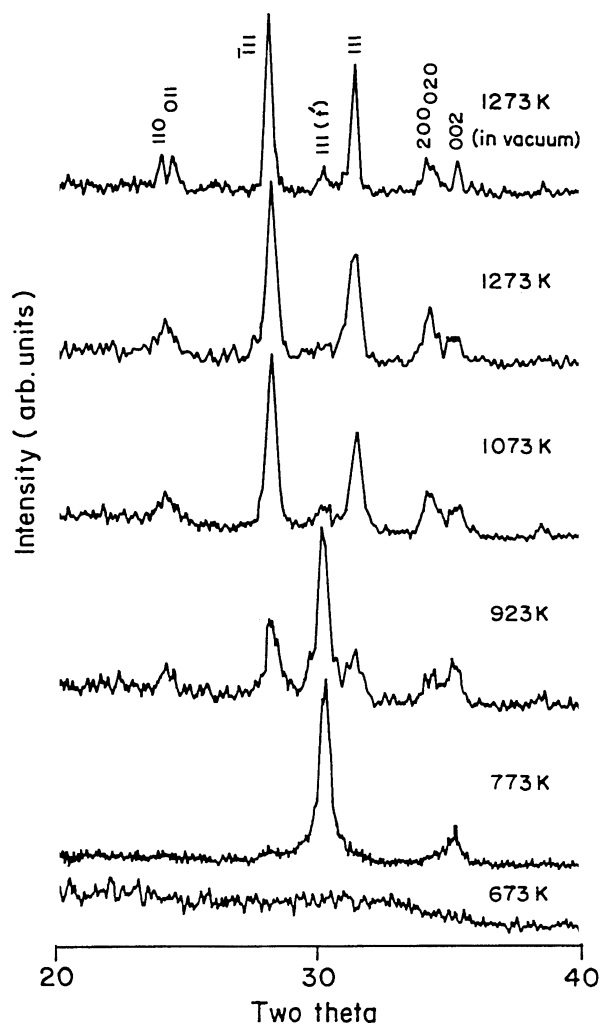
Fig. 4. XRD spectra of Z0H samples annealed at different temperatures.
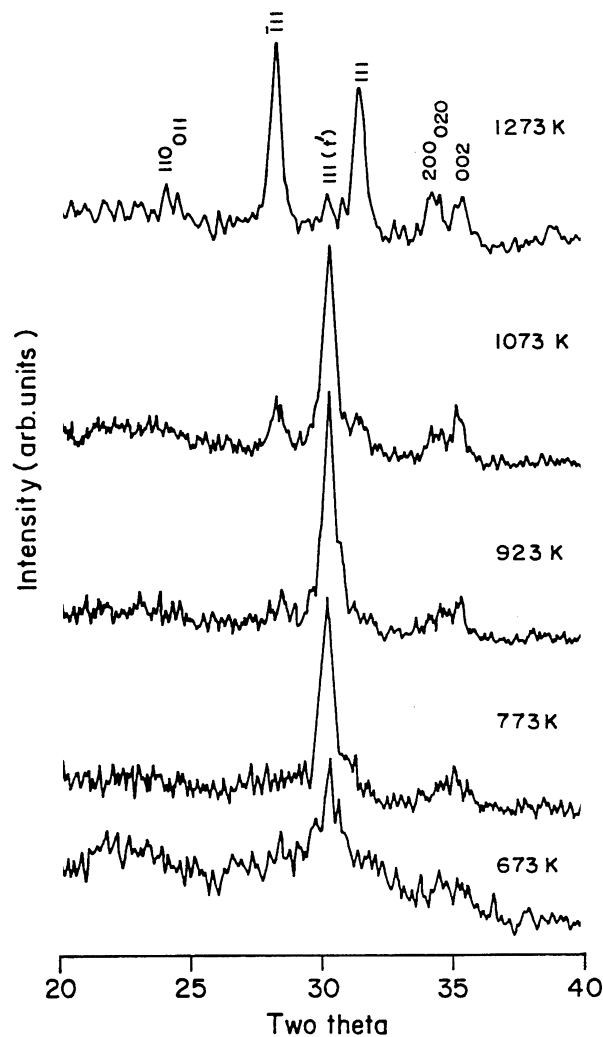
Fig. 5. XRD spectra of Z24H samples annealed at different temperatures.

may be attributed to the effect of structural defects giving rise to lattice strains in zirconia nanograins.

The metastable tetragonal phase of ZrO_2 has been discussed earlier[16] taking into account the defect states and chemistry of the materials. Keramidas et al.[10] have argued that in reality, the amorphous ZrO_2 is a bulk sample of crystal nuclei of structure very similar to that of the tetragonal ZrO_2 but with very limited long range periodicity; these nuclei serve as nuclei for the growth of metastable tetragonal ZrO_2 when the specimens are heated. On heating the sample, through a diffusionless transformation the inter-atomic distances change enough for the metastable tetragonal phase

to be formed. But in the present case the samples hydrolyzed for more than 48 h crystallize directly in the monoclinic phase in the as-prepared condition itself as inferred from Fig. 1. The driving force for crystallization in the course of hydrolyzis may be associated with the change in the internal energy of the colloids in the precursor solution. As the hydrolyzing time is increased, the aqueous solution transforms into a colloidal one absorbing the thermal energy supplied during the synthesis process. Since the process is very slow and carried out at low temperature (<423 K), the colloids crystallize with a short range order. For all the powders heat treated at 773 K for 1 h, the volume fractions of the tetragonal phase in each sample are found to decrease with the hydrolyzing time (T) as shown in Fig. 6. Now it is essential to understand the competing mechanisms which induce the nucleation of the monoclinic phase during hydrolyzis for $T > 48$ h.

Garvie[9] has attributed the formation of metastable tetragonal phase to the crystallite size effect via the excess surface energy of the small crystallites. In the present investigation, the average grain size decreases from 16 nm for the unhydrolyzed sample to 7 nm for the sample hydrolyzed for 48 h. On increasing the hydrolyzing time to 72 h and above, the grain size slightly increased up to 9 nm due to the nucleation of the colloid crystallites (Fig. 6). It is also noticed that with increasing hydrolyzing time, the volume fraction of the tetragonal phase decreases. It is worthwhile to note that though the grain size is below the critical size for the tetragonal to monoclinic transformation as observed by Garvie *et al.*[11] only the monoclinic phase is found to be dominant in Z48H, Z72H and Z140H samples.

4.2 Effects of thermal treatments

The variation of the volume fraction of the metastable tetragonal phase with the annealing temperature is shown in Fig. 7. It is interesting to note that the temperature regime of the metastability of the tetragonal phase is found higher in Z24H sample compared to that of the Z0H. The $t' - m$ phase transformation takes place in the temperature range 1073 to 1273 K in Z24H, but in Z0H, the transformation occurs between 873 and 1073 K. It is observed that when, the annealing temperature is increased from 773 to 1273 K, the grain size is found to increase from 16 to 24 nm in Z0H and from 12 to 19 nm in Z24H samples. Since both the samples exhibit different grain size for a given annealing temperature, it is noteworthy to correlate the grain size and the volume fraction of the t'-phase in Z0H and Z24H samples. The volume fraction of the t'-phase in both the samples is plotted with grain size in Fig. 8. It is clear that the $t' - m$ phase transformation takes place at certain grain size regime, in this case, it is around 18 mn.

On the other hand, in the case of Z72H and Z140H samples, some more additional effects are supposed to be dominant apart from the grain size effect. In our recent studies on nanocrystalline yttria stabilized zirconia (YSZ) by using high resolution electron microscopy, a large amount of elastic strains were observed which cause the lower symmetry monoclinic phase in the as-prepared powder to be formed after 140 h hydrolyzing.[17,18] Even though the yttria-zirconia solid solution would have been formed in the as-prepared
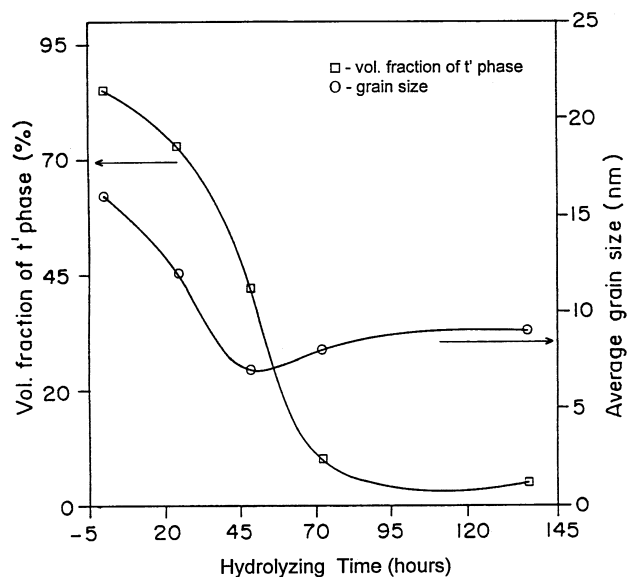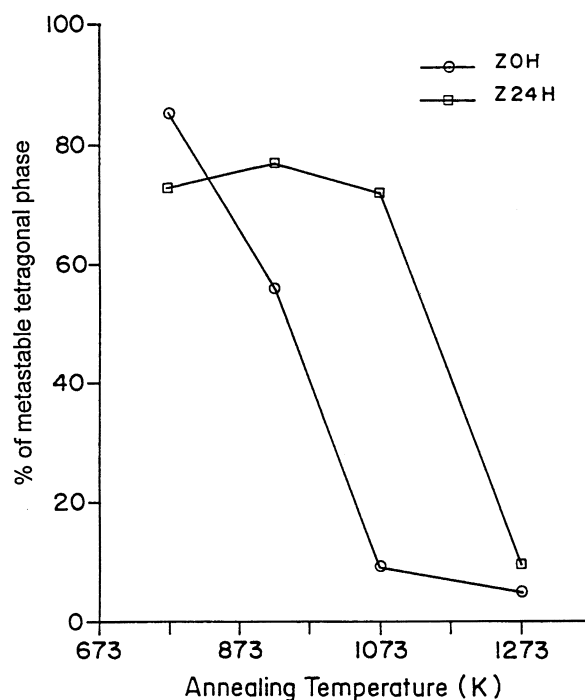
Fig. 6. The variation of volume fraction of the metastable tetragonal phase and grain size with hydrolyzing time after the powders are annealed at 773 K for 1 h.

Fig. 7. The variation of the percentage of metastable tetragonal phase with annealing temperature in Z0H and Z24H samples.

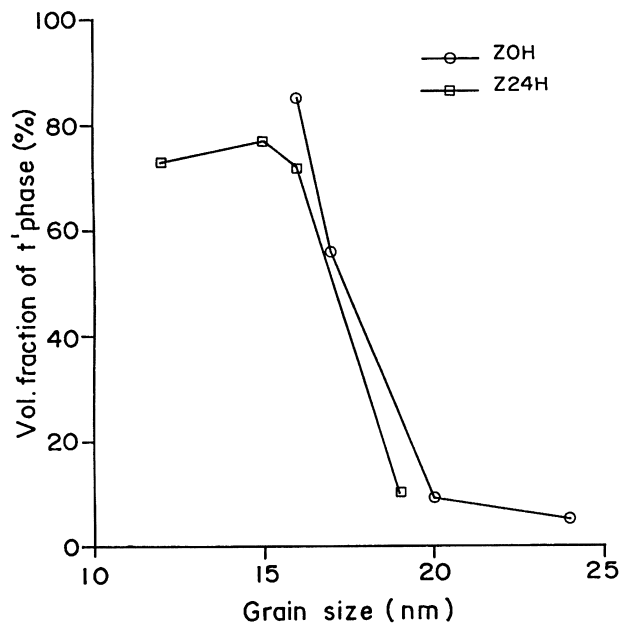**Fig. 8.** The percentage of t'-phase versus grain size in Z0H and Z24H samples.

5 Conclusions

The important conclusion of the present study is that there are two different structural routes, for the phase transformation in hydrolyzed ZrO_2: (i) amorphous to monoclinic phase transition with increasing hydrolyzing time and (ii) amorphous to metastable tetragonal and then to monoclinic phase transformation with increasing annealing temperature. It appears that the thermodynamics of the ZrO_2 powder is influenced by the long term hydrolyzis of the precursor solution. Even though an average critical grain size for the $t'-m$ phase transformation is found to exist, the defect states such as lattice strains and vacancy clusters in the grain assemblages are believed to alter the phase formation or stabilization process in the nanocrystalline ZrO_2.

condition itself, the effect of the longer hydrolyzing time results in lattice strains which cause the monoclinic phase to persist. But on heating the powder at $673\,K$ and above, the strains were removed and the tetragonal or cubic phase is stabilized depending on the yttria concentration. Thus, for longer hydrolyzing times, the grain size effect on stabilizing the tetragonal phase is overcome by the effect of lattice strains which cause the less symmetric monoclinic phase in the as-prepared powders.

For different preparation methods, the microstructure of nanomaterials can be nanocrystalline, nano-amorphous grain or nanocluster assemblages with some crystalline features. Since the grain boundaries are the basic components of nanomaterials, changes in their internal microstructure should inevitably change the physical and chemical properties. Yu et al.[19] have attributed the reduction in the crystal symmetry of nano-SnO_2 grain assemblages to the defects such as a large number of lattice vacancies at the interfaces, vacancy clusters and local lattice disorders on reducing the grain size to the nanometer regime. The origin of the lattice defects (strains) in the precipitated zirconia powder is still not clear. The cohesive energy of a tetragonal crystal is slightly less than that of the monoclinic structure by an amount approximately equal to the heat of transformation.[11] During hydrolyzis, the introduction of the lattice strains which are elastic in nature, might have gradually increased the lattice energy thus giving rise to the excess strain energy which induce the monoclinic phase to exist.

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