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Ultrafine-Grained Dense Monoclinic and Tetragonal Zirconia

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Nanoparticles of ZrO_2 with diameters ranging from 4 to 8 nm were synthesized by gas condensation. As-prepared *n*-ZrO_2 particles have a monoclinic and a high-pressure tetragonal structure depending on size. Pure ZrO_2 was sintered to full density under vacuum at $0.4T_m$ within the monoclinic phase field. Final grain sizes in theoretically dense pellets are below 60 nm. By sintering below the monoclinic–tetragonal transition temperature, microcracking was completely avoided. Tetragonal ZrO_2 stabilized with 3 mol% Y_2O_3 was prepared by interdiffusion of nanoparticles and sintered to near-theoretical density.

I. Introduction

Over the past years, there has been increasing interest in nanostructured (*n*-) ceramics for their lower sintering temperatures and improved mechanical properties. Among other synthesis techniques, gas condensation has been shown to yield clean nanostructured powders with extremely high surface areas which have good sinterability. Until now, extensive data have been obtained on *n*-TiO_2 and *n*-Y_2O_3. Recently, powders of *n*-ZrO_2, which is of technological importance, have been synthesized in small quantities by gas condensation using DC and RF sputter sources.[1,2]

Sintering of undoped monoclinic zirconia with conventional grain sizes to high densities by conventional consolidation techniques such as air and vacuum sintering has hitherto not been successful. The reason is that the temperatures necessary for sintering have always been well above the reversible monoclinic-to-tetragonal transformation, i.e., above 1170°C. The martensitic transformation during cooling is accompanied by a dilatational strain of 4.5%, causing microcracking.

Fabrication of high-density, monoclinic zirconia with minimal microcracking has been accomplished only by using doped zirconia. Sense *et al.* synthesized polycrystalline monoclinic ZrO_2–2% HfO_2 with a density of 5.77 g/cm^3, i.e., 99% of the theoretical value.[3] The nearly crack-free specimen was fabricated by a two-step process: hot pressing below 1000°C to a density of 4.22 g/cm^3 and then heating above 2250°C in a reducing atmosphere. Yoshimura *et al.* obtained near full density for the same chemical composition.[4] Garret and Ruh achieved densities of 95% by vacuum sintering at 2300°C for 3 h followed by reoxidation at 1000°C for 18 h.[5] Recently, Cutler *et al.* have stressed their inability to prevent microcracking in monoclinic zirconia.[6] In all cases reported in the literature, final grain sizes were in the micrometer range.

Therefore, it seems that the only means to synthesize dense, undoped zirconia with monoclinic structure is to modify the powder microstructure such that sintering temperatures are below the monoclinic-to-tetragonal phase transition. Previous experiments have clearly shown that sintering temperatures can be reduced dramatically by using nanostructured powders with particle/grain sizes less than 20 nm.[7] Additionally, in order to maintain nanometer-sized grains in fully dense ceramics, grain growth during sintering has to be controlled.

The present paper reports on the synthesis of nanostructured monoclinic ZrO_2 powders by gas condensation and their sintering below the m–t transformation temperature. In addition the sintering behavior of Y-stabilized tetragonal ZrO_2 has been studied.

II. Experimental Procedure

Nanostructured ZrO_2 powder was synthesized by gas condensation processing. This technique was originally proposed by Gleiter[8] and later modified using a postoxidation step for the synthesis of oxides.[9] The process consists of evaporation of zirconium monoxide in a helium atmosphere of 250 to 1500 Pa followed by postoxidation of deposited nanoparticles. The postoxidation is carried out at a controlled rate in order to avoid agglomeration of the highly reactive nanoparticles. As prepared oxide powders are annealed at 300°C in an oxygen atmosphere to obtain stoichiometric ZrO_2.

Compacts, 8 mm in diameter and 0.5 mm thick, were made by applying a uniaxial pressure in the range of 200 to 1000 MPa at room temperature. These pellets were sintered subsequently in air and under a vacuum of 4×10^{-4} Pa at several different temperatures for times ranging between 0.5 and 2 h. After vacuum sintering, the samples were annealed in flowing oxygen below the sintering temperature to establish stoichiometry. Additionally, sintering was studied *in situ* by dilatometry on cylindrical specimens. These samples with a diameter of 3 mm and a height of 3 to 4 mm were compacted at room temperature at uniaxial pressures up to 1 GPa. The relative length change during sintering was measured using a Netzsch dilatometer with a heating rate between 2 and 10°C/min. Density of the pellets was measured using Archimedes' principle and from the geometry and weight of the specimen.

Y-stabilized tetragonal ZrO_2 was prepared in the following way: a colloidal suspension containing *n*-ZrO_2 and 3 mol% of *n*-Y_2O_3 was formed in deionized water and treated ultrasonically to obtain good mixing and to break up weak agglomerates. The water was subsequently dried out. After compaction at room temperature samples were heated at 1000°C to obtain interdiffusion of the oxides and sintering.

III. Results and Discussion

(1) Powder Structure

X-ray diffraction shows considerable line broadening from which the grain size can be estimated using the Scherrer formula. The average grain size *d* depends on the He gas pressure during evaporation: *d* increases from 6 to 12 nm at 100 and 1000 Pa He pressure, respectively. This is in agreement with the observations reported by Granqvist and Buhrman for metallic nanoparticles.[10] The grain size distribution shown in Fig. 1 determined by dark-field TEM is lognormal and confirms the

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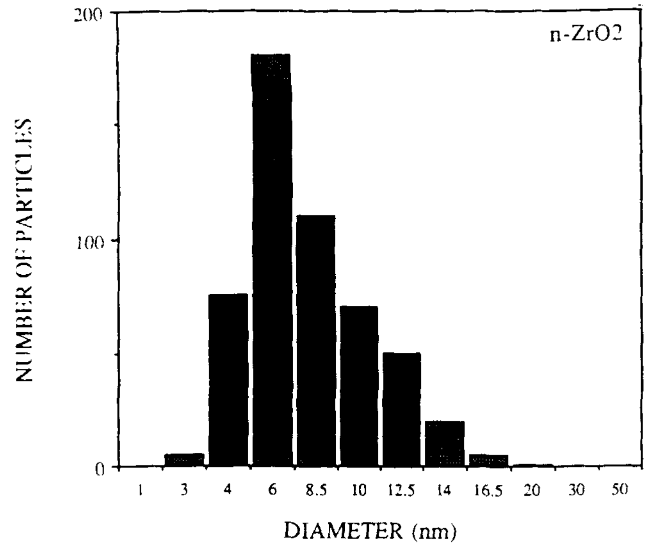

Fig. 1. *Grain size distribution of as-prepared nanostructured* ZrO_2 powder determined by dark-field transmission electron microscopy.

results of X-ray analysis. Figure 2 shows X-ray diffraction spectra of uncompacted n-ZrO_2 powder prepared at different gas pressures. Besides the peaks of the equilibrium monoclinic crystal structure of ZrO_2, lines of a second phase are also present. Detailed study using Rietvelt analysis[11] shows unambiguously that the second phase is a tetragonal high-pressure modification of zirconia.[12] Its stability in nanoparticles at ambient conditions can be explained by the Gibbs–Thomson effect as in the case of n-Y_2O_3.[13] An additional hydrostatic pressure Δp acts on the interior of small particles with radius r due to surface energy γ (in liquid particles) or surface stresses f (in solid particles): $\Delta p = \gamma$ (or f)/$2r$. According to the phase diagram given in Ref. 12 the high-pressure phase is stable at temperatures above 900°C and pressures exceeding 3 GPa. During exothermic postoxidation, ZrO particles heat up to high temperatures while a high pressure exists in the nanoparticles due to surface stresses. In the smallest particles the tetragonal modification is energetically favored while in larger particles of the distribution the monoclinic phase is more stable. This explains the coexistence of both phases in as-prepared powders. During subsequent rapid cooling of the nanoparticles the tetragonal modification is quenched in. However, even at high pressures and at room temperature, tetragonal ZrO_2 is not stable. On the basis of the high-pressure phase diagram and the Gibbs–Thomson effect, a critical particle size is expected below which the tetragonal phase is thermodynamically stable. As the average radius of the particles increases above a critical value, i.e., at higher He pressures, the internal pressure resulting from surface energy is not sufficient to stabilize the tetragonal phase and more particles of the distribution become monoclinic. On the basis of these considerations, the ratio of monoclinic to tetragonal phase should increase as particle size increases. This can be clearly seen in Fig. 2, a and b, by comparing the peak intensities of the monoclinic and tetragonal phases.

(2) Compaction of Powders

On compaction of n-ZrO_2 powder (even at small uniaxial pressures of the order of 10 MPa) the tetragonal phase transforms completely to the monoclinic modification as seen in Fig. 3. Since all sintering studies were performed after compaction at pressures greater than 200 MPa, essentially pure monoclinic ZrO_2 was used in all cases. Therefore, the presence of tetragonal phase in as-prepared pure ZrO_2 powders has no relevance for the sintering studies.

The densities of n-ZrO_2 compacted at room temperature range from 36% to 51% of the theoretical density of m-ZrO_2 depending on the applied pressure. From the plot of density vs compaction pressure shown in Fig. 4, it can be concluded that only weak agglomerates exist in the powder that are broken up during compaction. At low pressures these agglomerates do not break and lower packing efficiency results. As agglomerates are broken up with increasing pressure, better packing of particles results in increased initial density. But the more important reason why high pressures are needed to achieve green densities of 45% or so is the enormous frictional resistance between the nanoparticles which needs to be overcome. However, further increases of pressure beyond 600 MPa do not yield higher initial densities. As in the case of n-Y_2O_3, n-ZrO_2 samples compacted at room temperature are highly transparent to visible light even though the density is below 51%. This indicates that all pores are much smaller than the wavelength of light. TEM studies, small-angle neutron scattering,[14] and nitrogen adsorption measurements[15] show indeed that all pores are smaller than 10 nm. The small pores and narrow size distributions stem from the lack of agglomeration in n-ZrO_2 such that particle and grain

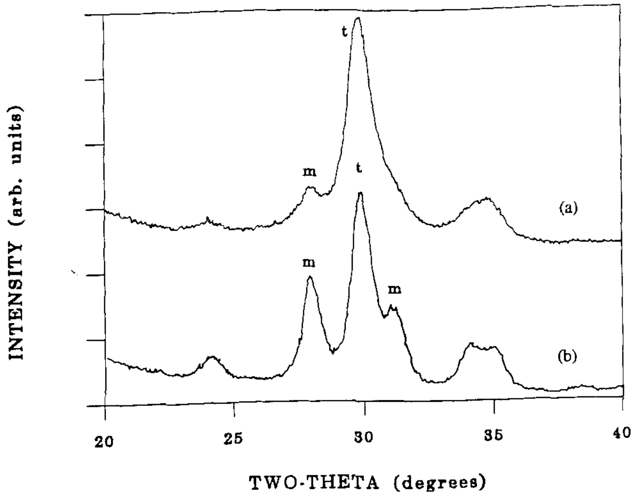

Fig. 2. X-ray diffraction spectra of uncompacted nanostructured ZrO_2 powder prepared at (a) 250 Pa with an average particle size of 4 nm and (b) 1500 Pa with an average particle size of 8 nm.

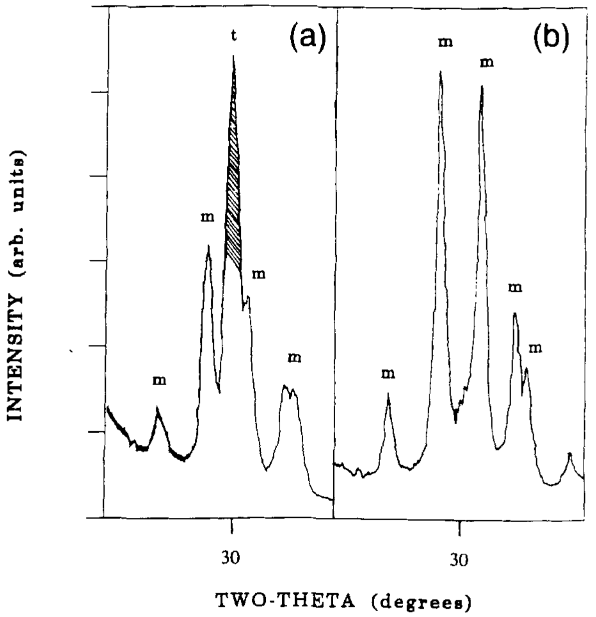

Fig. 3. X-ray diffraction spectra of (a) uncompacted nanostructured ZrO_2 powder and (b) compacted nanostructured ZrO_2 pellet. The compaction pressure was 50 MPa.

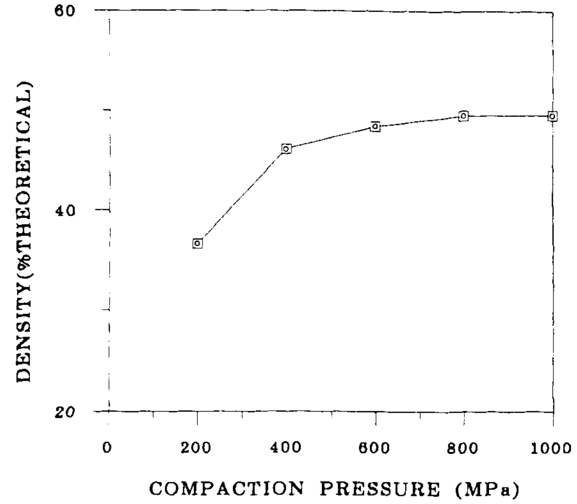

Fig. 4. Relative density of nanostructured ZrO_2 as a function of compaction pressure at room temperature.

sizes are comparable. This microstructure is desirable for sintering and can be achieved only by slow and controlled post-oxidation avoiding the exothermic heat release. As a consequence of the unagglomerated state of the powder, stable colloids can be formed by suspension of as-prepared powders in alcohols or water. This is a prerequisite for the effective mixing of oxides as colloids used to prepare Y-stabilized ZrO_2 (see discussion below).

(3) Sintering

Figure 5 shows sintering curves of n-ZrO_2 with an average particle size of 8 nm and a commercial Y-stabilized ZrO_2 ceramic (Nippon, 2.6 Y-TZP) measured by dilatometry. The temperature is raised at 2°C/min from room temperature to 1400°C to obtain high densities in n-ZrO_2 as well as in the commercial ceramic. The final density is achieved at 1200° and 1400°C in n-ZrO_2 and large-grained Y-stabilized t-ZrO_2, respectively. Sintering of n-ZrO_2 occurs at approximately half the melting point while commercial Y-stabilized ZrO_2 requires higher temperatures for densification. Densification of the commercial ceramic occurs over a narrow temperature regime between 1200° and 1400°C. However, shrinkage of n-ZrO_2 begins at temperatures as low as 600°C, i.e., $0.3T_M$. As in other nanostructured ceramics, diffusion processes become dominant and densification starts at much lower temperatures. Since the nanostructured sample transformed during heating and cooling, microcracking occurred, resulting in partially shattered samples. Consequently, the final density of n-ZrO_2 could not be determined in this experiment. The influence of initial grain size on densification can be seen in Fig. 6 comparing two n-ZrO_2 with 4- and 8-nm particle size. Clearly, densification starts at lower temperatures in the sample with smaller initial particle size. However, because of excessive grain growth at high temperatures (the grains have grown to about 60 nm at these temperatures, which is 15 times the initial particle size), final sintering temperatures are almost the same for both samples. Therefore, prevention or suppression of grain growth is a key issue in sintering of nanostructured ceramics to take full advantage of the increased reactivity of nanoparticles. This could be done by addition of grain growth inhibitors such as alumina.

In order to study densification behavior in more detail, sintering for 2 h was performed in air and under vacuum at temperatures ranging from 800° to 1150°C. Since total times were longer in these isochronal experiments than in the dynamic studies used in dilatometry, final sintering temperatures are lower.

Figure 7 shows the density of n-ZrO_2 as a function of temperature during sintering in air. A maximum density of 93.7% of theoretical is obtained at a sintering temperature of 1075°C. At higher temperatures density decreases as the sample forms microcracks due to tetragonal-to-monoclinic phase transformation during cooling. In contrast, sintering under vacuum for 0.5 h yields theoretical density, i.e., >99.9% at 1000°C. The reasons for the enhancement of sintering under vacuum compared to air are presently not clear. Avoiding entrapment of air in pores of a few nanometers,[14] which hinder densification and enhancement of diffusivity in nonstoichiometric ZrO_2, possibly contributes to the observed changes of densification rates. Loss of stoichiometry during vacuum sintering can be reverted by postannealing of the sintered parts in air at the sintering temperature. Since the sintering temperature is well below the m–t transformation, no microcracking occurs and theoretical densities are achieved. To the best of our knowledge this is the first time that pure ZrO_2 was sintered (in the absence of an external pressure) to theoretical density without microcracking.

Although grain growth inevitably accompanies densification, it has been found in vacuum-sintered n-ZrO_2 that the average grain size even in fully dense samples is below 60 nm. A plot of density vs grain size shown in Fig. 8 compares results for vacuum sintering of n-ZrO_2 with air sintering of n-Y_2O_3.[16] It can be clearly seen that grain growth is reduced in n-ZrO_2 because of the lower homologous temperatures T/T_m necessary for densification: n-ZrO_2 can be sintered at $0.4T_m$ while n-Y_2O_3 requires temperatures of $0.53T_m$.[17] Since the sintering temperature and

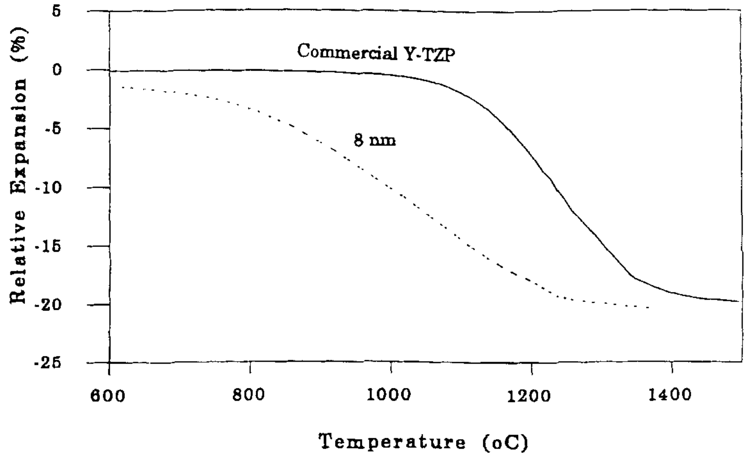

Fig. 5. Relative expansion of nanostructured ZrO_2 pellet, compacted at 400 MPa with an average particle size of 8 nm, and commercial Y-TZP, compacted at 100 MPa, determined by dilatometry.

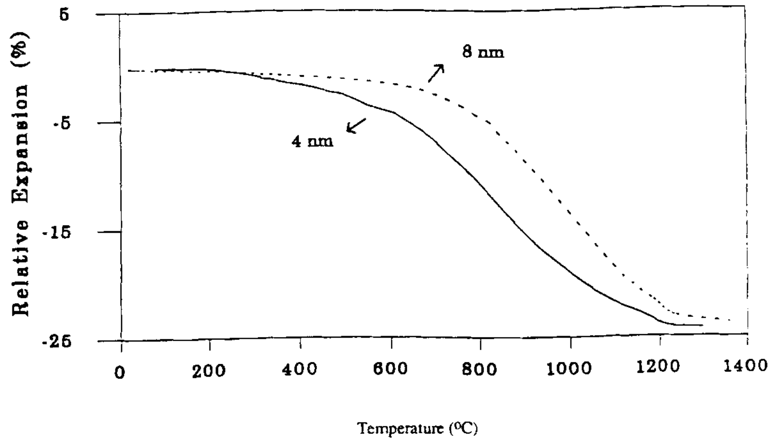

Fig. 6. Relative expansion curves for nanostructured ZrO_2 with initial particle sizes of 8 and 4 nm, determined by dilatometry. Samples were compacted at room temperature and 400 MPa.

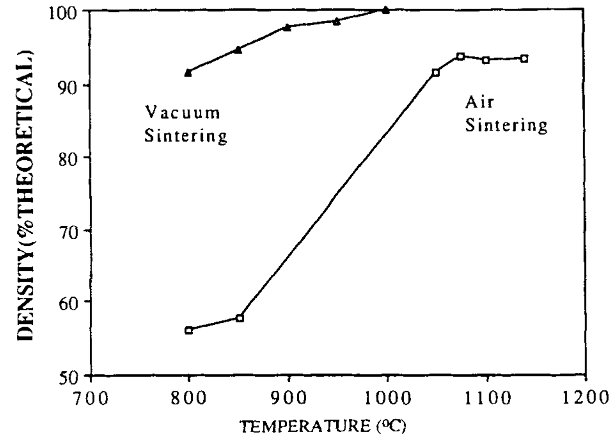

Fig. 7. Relative density of nanostructured ZrO_2 as a function of temperature for sintering in air (2 h) and under vacuum (0.5 h). Samples were compacted at room temperature and at a pressure of 400 MPa.

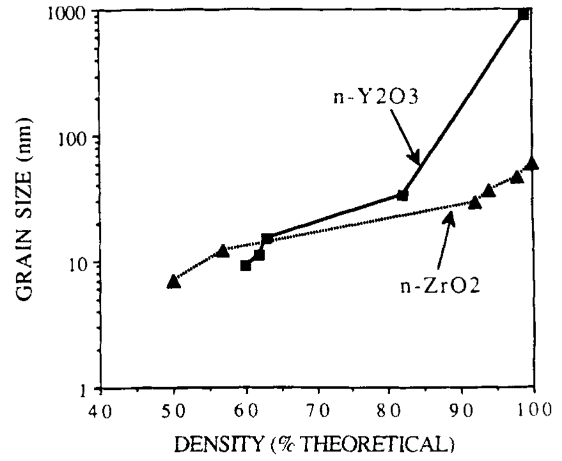

Fig. 8. Grain size as a function of relative density for vacuum-sintered nanostructured ZrO_2 and air-sintered Y_2O_3.

grain size are lower under vacuum as compared to air, this can be looked upon as an alternative to pressure-assisted sintering.[16]

However, further reduction of final grain size in dense ZrO_2 is necessary to study properties of *n*-ZrO_2 such as superplasticity or ionic conductivity. Consequently, alternative processing routes have to be employed. Previously, pressure-assisted sintering[6] and sinter-forging[18,19] have been used to obtain dense *n*-TiO_2 ceramics. Preliminary studies using *n*-ZrO_2 samples show that theoretically dense samples with grain sizes of 50 nm can be obtained by sinter-forging in air at 950°C, i.e., 50°C below the temperature used for vacuum sintering. Prior to sinter-forging the samples were presintered at 700°C, resulting in 70% density and 25-nm grain size. In an attempt to further decrease processing temperatures future work will involve vacuum sinter-forging. It is anticipated that sintering temperatures can be further decreased, resulting in smaller grain sizes. As a second alternative, pressure-assisted sintering under vacuum will be employed.

In many technological applications Y-stabilized tetragonal ZrO_2 is of interest. Since it is not possible to prepare nanostructured Y-TZP with the present gas condensation technique, an alternative route was used that is based on the unagglomerated state of the *n*-ZrO_2 and *n*-Y_2O_3 powders. Stable colloids of *n*-ZrO_2 and *n*-Y_2O_3 were formed in deionized water and mixed to obtain 3 mol% *n*-Y_2O_3 in *n*-ZrO_2. After drying and compacting, samples were sintered for 2 h at 1000°C in air, promoting interdiffusion and sintering. The compacted pellets were sintered under vacuum to full density in 2 h at 1000°C. X-ray diffraction of the sintered sample in Fig. 9 shows complete interdiffusion and transformation to tetragonal *n*-ZrO_2. Especially, no X-ray lines of Y_2O_3 are found. Short diffusion paths and high diffusion coefficients due to the small grain size and many interfaces promote fast interdiffusion. Additionally, contact of nanoparticles with solvents such as water seems not to affect subsequent densification. Thus, the technique of mixing nanoparticles of two or more ceramics and subsequent interdiffusion and sintering can be used to prepare complex ceramic materials.

IV. Conclusions

(i) Nanoparticles of monoclinic and tetragonal ZrO_2 with grain sizes ranging from 4 to 8 nm can be prepared by gas condensation. At low compaction pressures tetragonal structure transforms to monoclinic.

(ii) In the smallest grains of the particle size distribution, a nonequilibrium high-pressure tetragonal modification is found. At low compaction pressures, the tetragonal structure transforms to monoclinic.

(iii) Monoclinic *n*-ZrO_2 can be sintered under vacuum to theoretical density at 1000°C, i.e., below the monoclinic-to-tetragonal transformation, with a final grain size of 60 nm. Microcracking can be avoided completely.

(iv) Y-stabilized tetragonal *n*-ZrO_2 is prepared by mixing *n*-ZrO_2 and *n*-Y_2O_3 with a subsequent interdiffusion and sintering treatment.

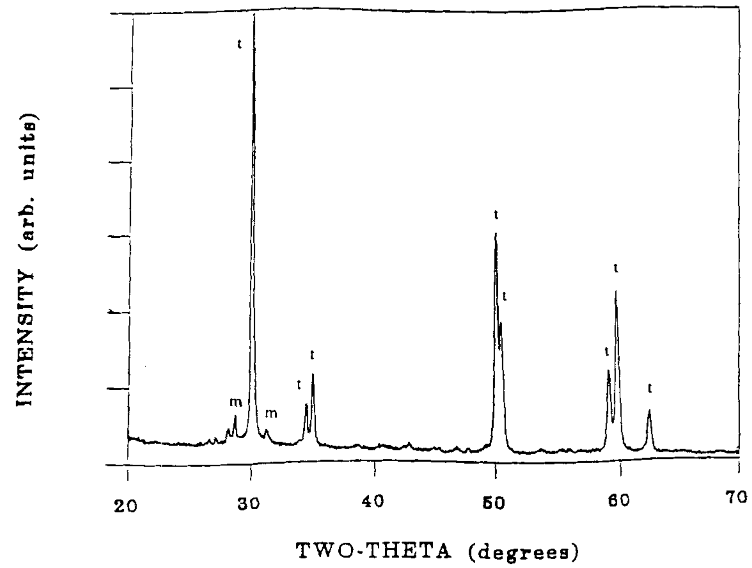

Fig. 9. X-ray diffraction spectra of a mixture of nanostructured ZrO_2 and 3 mol% Y_2O_3 compacted at room temperature and 400 MPa and subsequently sintered at 1000°C in air for 2 h. All major peaks belong to the tetragonal phase.

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