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Phase Characterization and Grain Size Effects of Nanophase Y_2O_3, ZrO_2 and Y_2O_3-ZrO_2 Composites Produced by the Gas-Phase Condensation Technique*

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PHASE CHARACTERIZATION AND GRAIN SIZE EFFECTS OF NANOPHASE Y_2O_3, ZrO_2 AND Y_2O_3-ZrO_2 COMPOSITES PRODUCED BY THE GAS-PHASE CONDENSATION TECHNIQUE

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ABSTRACT

Nanophase (n-) ZrO_2 was produced in its pure and partially stabilized form by the gas-phase condensation method. The material was examined by x-ray diffraction and Raman scattering to obtain information on the structural evolution of the material during sintering. Two types of Y_2O_3 doped ZrO_2 nanophase materials were made one by co-deposition of n-Y_2O_3 and n-ZrO_2 in a consecutive manner and the second by mechanically mixing n-Y_2O_3 and n-ZrO_2. We have determined that the co-deposition process is the most effect means of doping the n-ZrO_2.

INTRODUCTION

Nanophase materials, made from the assembly of physically or chemically produced clusters or nanocrystals have gained much attention in recent years [1-4]. Much of the interest in this area surrounds the enhanced or unique material properties when compared to bulk single crystal or coarse polycrystalline equivalents. In a more focused area of this growing field, nanophase oxide ceramics produced by the gas-phase condensation (GPC) process [1,4-6] have exhibited high densification and increased ductility at temperatures below half their melting point ($T < 0.5T_m$). These and other unique features of nanophase ceramics could lead to the development of near-net-shape-forming of ceramic parts and components. The development of this kind of technology could aide in reducing the expensive machining cost to reach net-shape in ceramic component production. Recent studies [7] have shown that GPC produced nanophase materials can be fabricated with an ultrafine microstructure, or nanostructure, with grains *and* pores below 20 nm. The nanostructure was evident from the high degree of transparency these samples exhibited, indicating that the size of the nanostructure was well below visible light-scattering wavelengths.

The synthesis of GPC produced nanophase ceramics has been limited to monolithic oxide materials. In order to advance the area of nanophase materials, especially via the GPC route, one needs to understand and evolve the synthesis of multicomponent and even heterogeneous nanophase materials (nanocomposites). Research in nanocomposites is currently yielding very interesting material properties, but most of these have been predominately produced by chemical means [8].

We have examined the formation of nanophase partially stabilized zirconia (PSZ) by the GPC process. As a monolithic material, zirconia is of little technical importance, and only by full or partial phase stabilization does zirconia become a useful material. The quality of partially or fully stabilized ZrO_2 is highly dependent on the dispersion of a cubic-structured stabilizer (e.g., MgO, CaO, Y_2O_3). Several techniques are used to achieve a uniform dispersion of the stabilizer including CVD coating of ZrO_2 particles and co-precipitation of hydroxides onto the ZrO_2 particles [9]. The motivation for studying doped n-ZrO_2 is to demonstrate that the GPC process can yield both a well dispersed mixture of heterogeneous oxides (ZrO_2 and Y_2O_3), and through heat treatments form solid solutions (PSZ). We will demonstrate that GPC co-deposition method is superior to mechanical mixing of the constituent nanophase powders.

EXPERIMENTAL

The GPC technique for making nanophase materials has been described in a variety of review papers in this area [4]. Essentially a precursor material is evaporated into a low pressure background (1-5 torr) of inert gas which causes condensation of the precursor vapors into nanocrystals. Depending of the parameters of the system, nanocrystals as small as 5-8 nm can be formed [7]. The basis for this investigation was to co-deposit nanophase ZrO_2 and Y_2O_3 in a consecutive manner to obtain an intimate mixing of the two materials. For this purpose a large

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surface area cold plate was used to thermophoretically collect the two materials. The cold plate was placed within 20 cm of the evaporation source and maintained at a temperature of 77K. Consecutive evaporations of Zr and Y were deposited as nanocrystals onto the cold plate. Once the process was complete the inert gas was removed and pure O_2 gas was released into the system. An exothermic reaction of the O_2 with the metallic nanocrystals formed the oxides ZrO_2 and Y_2O_3. The cold plate was heated in the O_2 environment to complete the oxidation. The loose powders were then scraped from the collector cold plate for analysis and processing.

The amount of Y_2O_3 doping was adjusted by the amount of Y metal evaporated from the source. Because the thermophoretic collection efficiency is low in this system, special care was taken to determine the collection yields of both materials so that the desired doping level could be determined. The average collection yields of ten ZrO_2 samples and fifteen Y_2O_3 samples were determined prior to the co-evaporation experiments. These average yields were used to calculate the appropriate amount of precursor material to evaporate to obtain a target doping level of 3 mole% Y_2O_3 in ZrO_2. At 3 mol%, we should have formed the "transformable" tetragonal phase [9].

A second PSZ material was made by mechanically mixing the powders of nanophase ZrO_2 with nanophase Y_2O_3 . Because the aggregates in GPC nanophase materials appear to break-up upon consolidation [7], the action of mechanically mixing and lightly milling the two materials may produce a homogeneous mix. The two powders, ZrO_2 with 3 mol% Y_2O_3, were mechanically mixed in a V-blender for 24 hrs with a Teflon mixing media.

X-ray diffraction (XRD) measurements were done on a Rigaku x-ray diffractometer using Cu-K_α radiation from a rotating anode. Micro-Raman scattering experiments-were obtained using a Coherent Innova 70 Ar^+ ion laser and a Jobin-Yvon U-1000 Raman spectrometer with a single channel RCA C31034A photomultiplier tube as the detector in photon counting mode. The slit widths were set to yield 0.5 cm^{-1} spectral resolution. The incident laser light (487.9 nm at 50 mW) was incident on the sample through an optical microscope (X100 objective) to a spot size of ~1 μm in true 180° backscattering geometry with the scattered light dispersed by the monochromator. In addition, transmission electron microscopy (TEM), electron dispersion spectroscopy (EDS), and BET nitrogen absorption were also used to characterize the powders for grain size, purity, and surface area, respectively.

RESULTS AND DISCUSSION

The pure and doped powders were found to have an average nanocrystal size of 8 nm as determined by TEM. The BET surface area of the pure ZrO_2 powder was 150 m^2/g and the co-deposited Y_2O_3 doped powder was 83 m^2/g. Both pure and Y_2O_3 doped powders were individually consolidated in dies into 1.27 cm diameter, 0.5-2 mm thick pellets. Consolidation pressures of 10-20 Kpsi were applied at room temperature. Both the pure and Y_2O_3 doped nanophase materials showed significant transparency when placed on a contrasting black/white background [7]. From the similarity in transparency in both the pure and doped samples we can qualitatively infer that the doped samples have a good level of mixing, i.e., there are no large regions in the sample where refractive index mismatch could produce light scattering and opacification. An EDS analysis using an EDAX probe showed that the relative amount of yttria in co-deposited sample was less than the mechanically mixed sample. Using the known 3 mol% doping level of the mechanically mixed sample as a compositional standard, we estimate a doping level of 1.5 to 2.0 mol% Y_2O_3 in the co-deposited sample.

The phase characteriztion and grain-size effects in pure nanophase Y_2O_3 [10] has been previously reported. X-ray diffraction analysis of n-Y_2O_3 in the as prepared state have shown that the monoclinic γ-Y_2O_3 phase with a=0.1391 nm, b=0.3483 nm, c=0.859 nm, $\alpha=\beta=90°$ and $\gamma=100.15°$ is stabilzed in the as-prepared state. This structure, with the symmetry group C2/m, is known as the high pressure modification of yttria which has been obtained by application of a hydrostatic pressure of 2.5 GPa at 1000°C [11]. The density of the monoclinic phase is 5.50 g/cm^3, while cubic yttria has a density of 5.01 g/cm^3. Helium gas pycnometry of the loose as-prepared powder yields a bulk density of 5.55 g/cm^3 which supports the monoclinic γ-Y_2O_3 phase identification. Particle sizes determined from line broadening by using the Scherrer formula [12] yield average grain sizes of 8 nm in excellent agreement with the TEM results [13].

Micro-Raman scattering was employed in order to confirm the x-ray results and to determine the possible presence of other phases. Fig. 1a shows Raman spectra of cold pressed sample of a) conventional α-Y_2O_3 with grain sizes in the micrometer range, and b) as-prepared n-Y_2O_3. While the as-prepared oxide shows evidence of a small fraction of the cubic phase (from the weak phonon mode at 377 cm^{-1}), the dominant Raman-active modes in this material

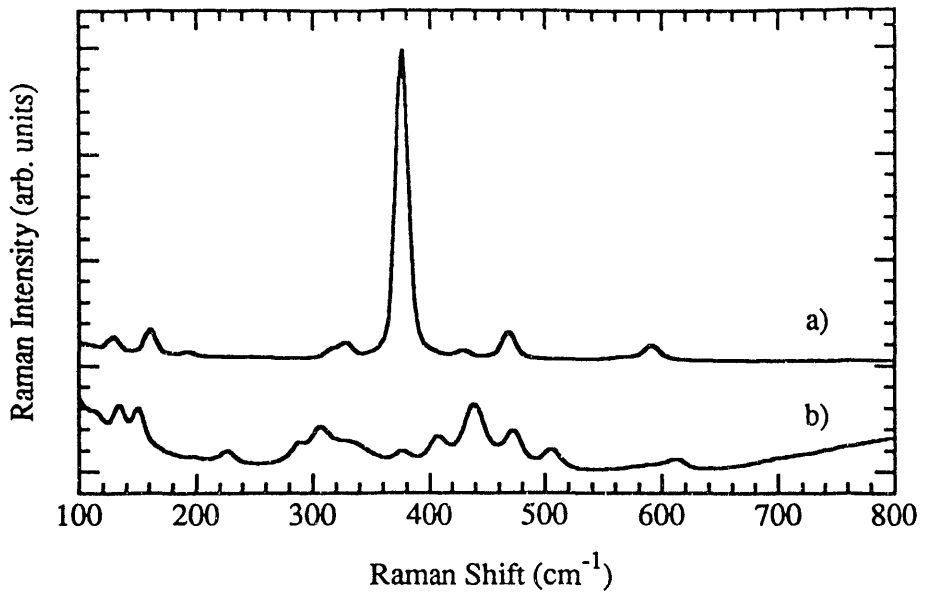

Figure 1: Microprobe Raman spectra of a) conventional and b) as-prepared nanostructured Y_2O_3.

are clearly distinct from that of α-Y_2O_3. To our knowledge, Fig. 1b shows the first reported Raman spectrum of the high pressure phase of γ-Y_2O_3.

The presence of the denser, high-pressure phase, γ-Y_2O_3, at ambient conditions can be readily explained by the Gibbs-Thompson effect [14]. The surface curvature of the nanometer-sized particles results in a hydrostatic pressure component Δp on the interior of the particles with a radius D which is related to the surface/interface energy γ: $\Delta p = 4\gamma/D$, where γ is the surface/interface energy. If this pressure component is high enough (e. g. below a critical particle diameter) high pressure phases with higher density will become favorable. The Gibbs-Thompson pressure in n-Y_2O_3-particles with an average particle diameter of 8 nm can be estimated as follows. Since the surface energy of nanostructured Y_2O_3 is not known, a value of 1500 mJ/m^2 typical for ceramics is assumed. A pressure increase of $\Delta p=1.5\times10^9$ Pa (15 Kbar) is calculated, which is the right order of magnitude for the pressure induced phase transformation reported in yttria.

To obtain a baseline set of data, pure nanophase and conventional coarse grained (> 1 μm) monoclinic ZrO_2 were examined first. Figure 2a shows the 2θ XRD analysis of as-pressed conventional and as-pressed and sintered nanophase ZrO_2. Sintering was performed at temperatures of 600°C, 800°C, 1000°C, and 1200°C. All sintering times were for 1 hour except for the 1200°C sample which was sintered for 6 hours to fully evolve the sample microstructure. We attribute the spectral difference between the as-pressed and sintered samples to an increase in the materials crystallinity during sintering. Figure 2a shows that the nanophase ZrO_2 is dominated by the monoclinic phase, but there appears to be a small amount of tetragonal phase ZrO_2 (T) present in the sample.

Two possible reasons for the presence of tetragonal phase ZrO_2 in the nanophase samples can be attributed to (i) phase stabilization by cubic tungsten oxide impurities that could have resulted from the evaporation process[15], or (ii) a grain size effect[16]. The phase change from impurities is unlikely since the tetragonal phase disappears at high sintering temperatures and no tungsten (or other) impurities were found to be present at any substantial level. It is more plausible that the presence of tetragonal ZrO_2 is due to the nanometer grain structure within the consolidated samples. The presence of tetragonal ZrO_2 in a material with an average grain size of 5-8 nm is not unexpected[16]. It is evident from Figure 1 that the tetragonal phase is not detectable in the 1200°C sintered sample. Using the x-ray line broadening as an indicator of grain size, one also observes that grain size is stable in the samples sintered to 1000°C until 1200°C where the peaks tend to sharpen from the onset of rapid grain growth. The coincidental onset of grain growth and the disappearance of the tetragonal phase suggests a grain size effect is occurring.

The Raman scattering spectrum of as-pressed and sintered nanophase ZrO_2 is shown in Figure 2b. The Raman spectrum, like the XRD spectrum, is dominated by the monoclinic phase[17]. The tetragonal phase of ZrO_2 has a weaker scattering cross section than the

monoclinic phase, making it more difficult to identify using Raman scattering. In addition, the as-pressed sample showed a strong, broadband photoluminescence component [18] that diminished after sintering at 600°C. This was also attributed to the development of the crystallinity of the sintered samples.

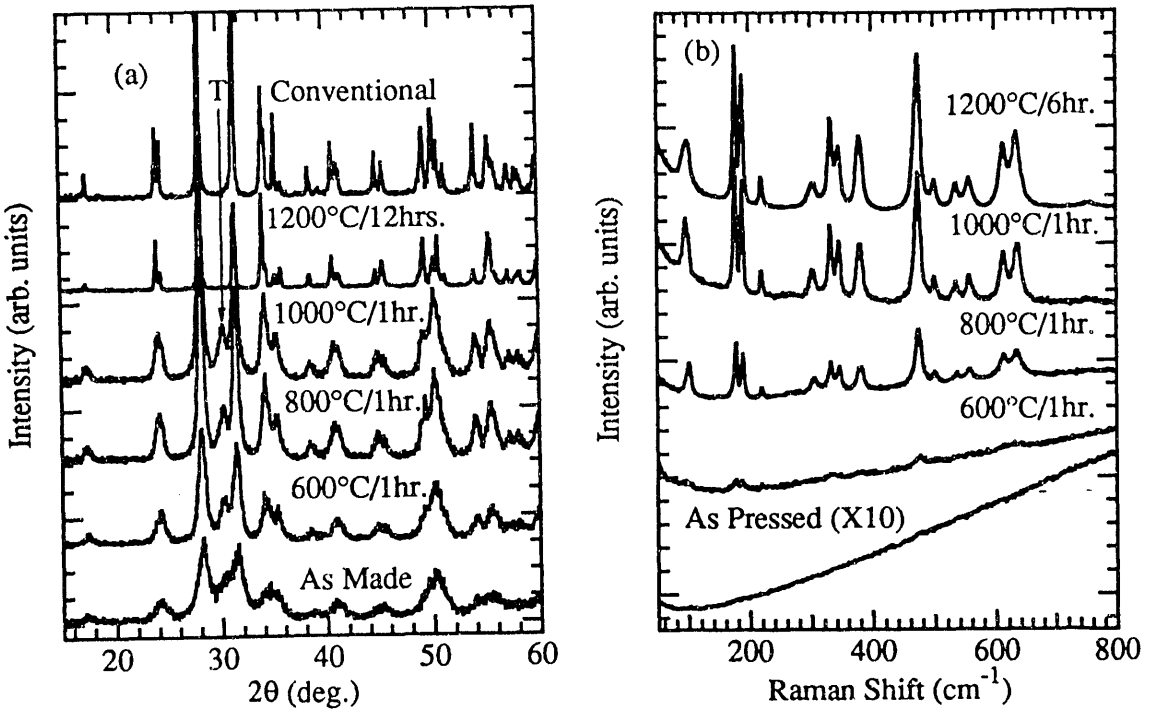

Figure 2. X-ray diffraction 2θ spectra (a) of undoped commercial coarse grained (conventional) and GPC produced n-ZrO_2 sintered at various temperatures. All peaks are attributed to the monoclinic phase of ZrO_2 with a small component of tetragonal (T) phase ZrO_2. Phase indentificaion made from a JCPDS CD-ROM database. Raman spectra (b) of undoped n-ZrO_2 sintered at various temperatures. The spectra are all attributed to the monoclinic phase of ZrO_2.

Having obtained baseline information on pure nanophase ZrO_2 we began an analysis of the nanophase PSZ material. Because of the spectral similarity with monoclinic ZrO_2 it is difficult to quantify the Y_2O_3 content by XRD or Raman. However, the Y_2O_3 will phase change to a distinguishable cubic structure at T > 600°C[10]. Figure 3 shows the 2θ, XRD spectra of the PSZ material prepared by co-deposition (Figure 3a) and mechanical mixing (Figure 3b). The as-pressed spectrum of both samples are very similar, showing a dominance in the monoclinic phase. Much like the pure nanophase ZrO_2 sample, both the as-pressed co-deposited and mechanically mixed PSZ material show the presence of tetragonal ZrO_2 as indicated (T) in the figure. Both a grain size effect and the possibility of phase change by doping may be the cause for the presence of tetragonal ZrO_2. The samples sintered at T > 600°C indicate the presence of cubic Y_2O_3 (Y) within the co-deposited and mechanically mixed samples. There is only a small change in the amount of tetragonal ZrO_2 in the samples sintered at T < 1200°C indicating that substantial solid state diffusion has not taken place. Sintering for 1 hr at 1200°C shows an increase in the tetragonal phase in the co-deposited PSZ sample with a corresponding decrease in cubic Y_2O_3 indicating the formation of a solid solution. The mechanically mixed PSZ sample shows no increase in tetragonal ZrO_2 with the cubic Y_2O_3 content remaining the same. Sintering of the co-deposited and mechanically mixed samples at 1200°C for 12 hrs shows further evolution of the tetragonal phase in the co-deposited sample while the mechanically mixed sample showed no increase.

Micro-Raman analysis of the PSZ samples sintered for 1 hour at 1200°C showed distinct differences between the co-deposited and mechanically mixed samples. A beam spot of 1 μm was used to probe each sample in various regions to examine the homogeneity. From this analysis it was quite evident that the co-deposited sample was homogeneous on a microscopic scale, with all spectra having the same relative peak intensities. A typical spectrum obtained on the co-deposited, 1200°C sintered sample is shown in Figure 4a. The peaks attributed to the different compositions and phases are indicated. The mechanically mixed sample exhibited a fair

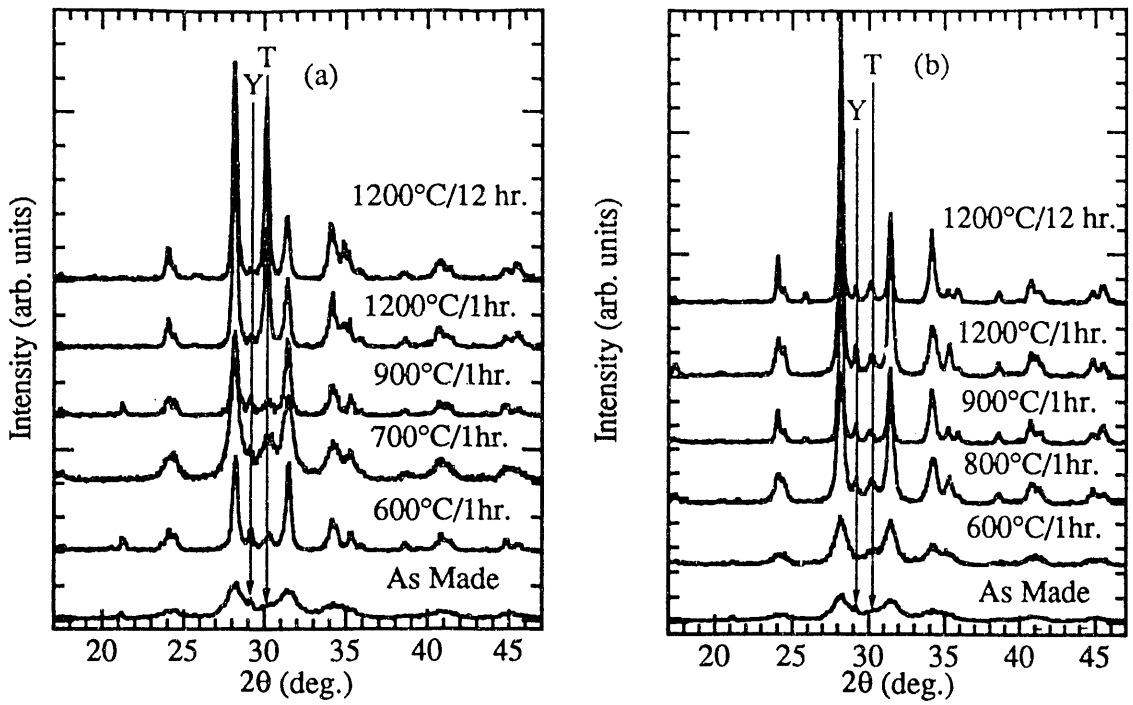

Figure 3. X-ray diffraction 2θ spectra of (a) co-deposited and (b) mechanically mixed Y_2O_3 doped ZrO_2 sintered at various temperatures. The peaks attributed to the tetragonal (T) phase of ZrO_2 and cubic Y_2O_3 (Y) are indicated.

degree of spatial inhomogeneity in its cubic Y_2O_3 and tetragonal ZrO_2 content. Figure 4b and 4c show the Raman spectra of two regions of the mechanically mixed sample. It is clear that the relative intensities of the spectral peaks at 380 cm^{-1} and 266 cm^{-1} indicate that varying amounts of cubic Y_2O_3 and tetragonal ZrO_2, respectively, can be detected. A quantitative analysis is however, very difficult because there are actually two phases contributing to the peak at 380 cm^{-1}, monoclinic ZrO_2 and cubic Y_2O_3.

It is evident from the above results that the GPC co-deposition technique has yielded a more homogeneous PSZ material than the mechanically mixed nanophase material. Both XRD and Raman scattering confirm that the co-deposited material has a higher and more homogenous content of tetragonal ZrO_2. This greater degree of stabilization occurred in the co-deposited samples despite the significantly lower doping level achieved by the co-deposition technique. The weak agglomeration of particles and high surface area obtainable with GPC nanophase ceramics are key ingredients to having a highly sinterable PSZ material. By obtaining better control over the composition during co-deposition synthesis, the results from this study suggest that the GPC produced PSZ has characteristics similar to the best commercially produced PSZ. Coupling the quality of the GPC co-deposited material (weak agglomeration and high surface area) with the ability to process the material in its as-synthesized form alleviates the sometimes delicate processing steps required for chemically produced powders (e.g., calcination steps for decomposition of chlorides or nitrates) [9].

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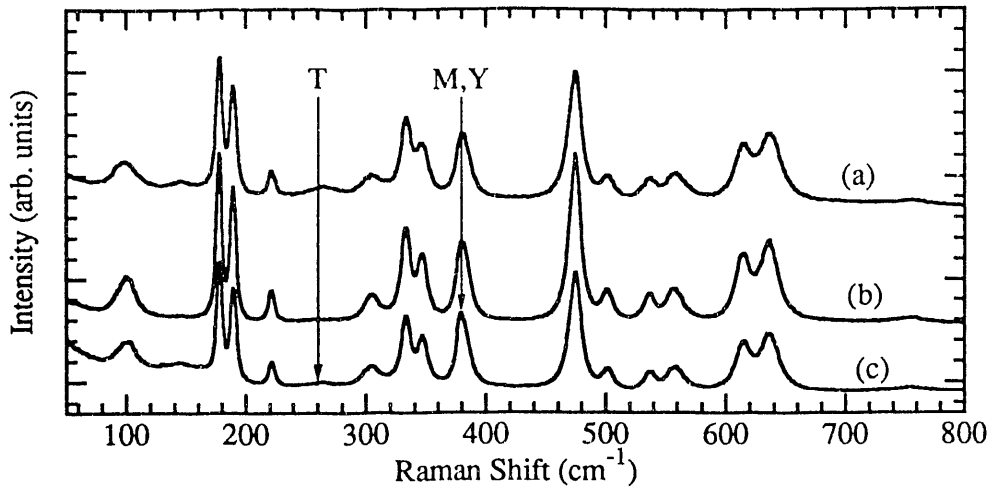

Figure 4. Micro-Raman spectra of (a) co-deposited and (b, c) mechanically mixed Y_2O_3 doped ZrO_2 sintered at 1200°C for 1 hour. The two spectra shown in 5b and 5c were taken 5 μm apart within the mechanically mixed sample. Beam spot diameter was estimated at 1 μm. The peaks attributed to the tetragonal (T) phase of ZrO_2 and cubic Y_2O_3 (Y) are indicated.

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