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ABSTRACT

Doping Rare-earth (RE) elements to ZrO₂ helps stabilize the cubic and tetragonal phases and improves resistance to thermal shock and sintering at high temperatures. Since a RE ion has a lower valency (3⁺) than Zr ion (4⁺), oxygen vacancies are formed to preserve electroneutrality. We have studied the crystal structure of La_{0.1}Zr_{0.9}O_{1.95} and Nd_{0.1}Zr_{0.9}O_{1.95} by neutron diffraction and examined the associated oxygen defects by a Fourier transform of the filtered residual diffuse scattering. The hydration process was investigated by inelastic neutron-scattering measurements of the hydrogen vibrational density of states of the surface hydroxyl groups and physisorbed water on these fine powders. We compare the O-H stretch vibrations for samples from with only surface hydroxyl groups to multilayer coverage of water molecules. The decreasing energies and increasing widths of the O-H stretch bands with increasing H₂O coverage indicate the influence of hydrogen bonding on the motion of water molecules. Similar elastic and inelastic experiments were also performed on a high surface-area pure ZrO₂ powder.

INTRODUCTION

Zirconia is widely used as a catalytic support of metallic active components in a variety of chemical processes. Adding a few mol. % of certain rare-earth (RE) element as a promoter to zirconia may enhance thermal stability and prevent sintering of the material at high temperatures because the cubic and tetragonal phases can be stabilized in RE modified ZrO₂. In order to achieve a large surface area as required for an effective catalytic support, these materials are usually prepared by a low-temperature processing method starting from mixing multi-component molecular precursor solutions. Recently, Ozawa and Kimura¹ reported the preparation of high surface-area (~80 m²/g) RE modified ZrO₂ powders using a method of coprecipitation from aqueous solution of zirconium oxychloride and rare earth chlorides followed by heat treatments. The enhancement of CO oxidation activity employing an iron catalyst supported by Nd-modified ZrO₂ makes it potentially useful in automotive exhaust catalytic converters. ¹ The crystal structures, phase transitions, surface area, and grain growth of La- and Nd-ZrO₂ at elevated temperatures have been characterized.^{1,2} Our continuing study of RE-ZrO₂ is motivated by several considerations. First, the multi-phased crystal structure of partially stabilized RE-ZrO₂ was not known precisely from previous x-ray measurements. Second, since the dopant cations (3⁺ rare-earth ions) have a lower valency than the Zr (4⁺) ions, oxygen vacancies are formed to preserve the overall electronic neutrality of the lattice. Third, high surface-area zirconia always adsorbs moisture in ambient atmosphere and forms hydroxyl groups covering the external and internal surfaces of the fine particles. The modification of the acidity of the surface lattice sites, including those associated with oxygen vacancies, has important consequences to the eventual performance of the catalytic system. In this paper we report the progress of neutron-diffraction studies of the crystal structure and short-range oxygen defects, and an neutron spectroscopic characterization of the surface OH groups and adsorbed water on La- and Nd- modified ZrO₂. In order to discern the effects induced by oxygen defects, similar measurements were also performed on a high surface-area pure ZrO₂ powder.

CRYSTAL AND DEFECTS STRUCTURES

The neutron-diffraction measurements at room temperature on La_{0.1}Zr_{0.9}O_{1.95} (heat treated to 600° C), Nd_{0.1}Zr_{0.9}O_{1.95} (heat treated at 600 and 800° C), and pure ZrO₂ were carried out

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using the General Purpose Powder Diffractometer (GPPD) at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. Details of the synthesis of RE-ZrO₂ samples were given elsewhere.¹ The preparation of the pure ZrO₂ powder initiated from a hydrolysis of aqueous zirconium oxychloride at 100° C for 78 hrs. An agglomerate, formed by addition of ammonia solution, was filtered and washed by distilled water, then washed by isopropylalcohol, and dried at 60° C for two days. The high surface-area ZrO₂ powder was obtained after heating at 290° C in air for 3 hrs. It has an BET-surface area determined by nitrogen adsorption of about 107 m²/g.

Fig. 1 displays the observed, background-subtracted and the fitted powder pattern over the 0.7-1.5 Å d-spacing range for the Nd_{0.1}Zr_{0.9}O_{1.95} sample heated at 800° C. Assuming a random substitution of the Zr atoms by Nd, a Rietveld analysis satisfactorily describes all the Bragg peak intensities for a major tetragonal (75%) and a minor cubic (25%) phase (weighted R-factor 6.0%). However, two features are noteworthy. First, the peaks are significantly broadened by the effects of small (~30 nm) grain sizes and large compositional fluctuations of

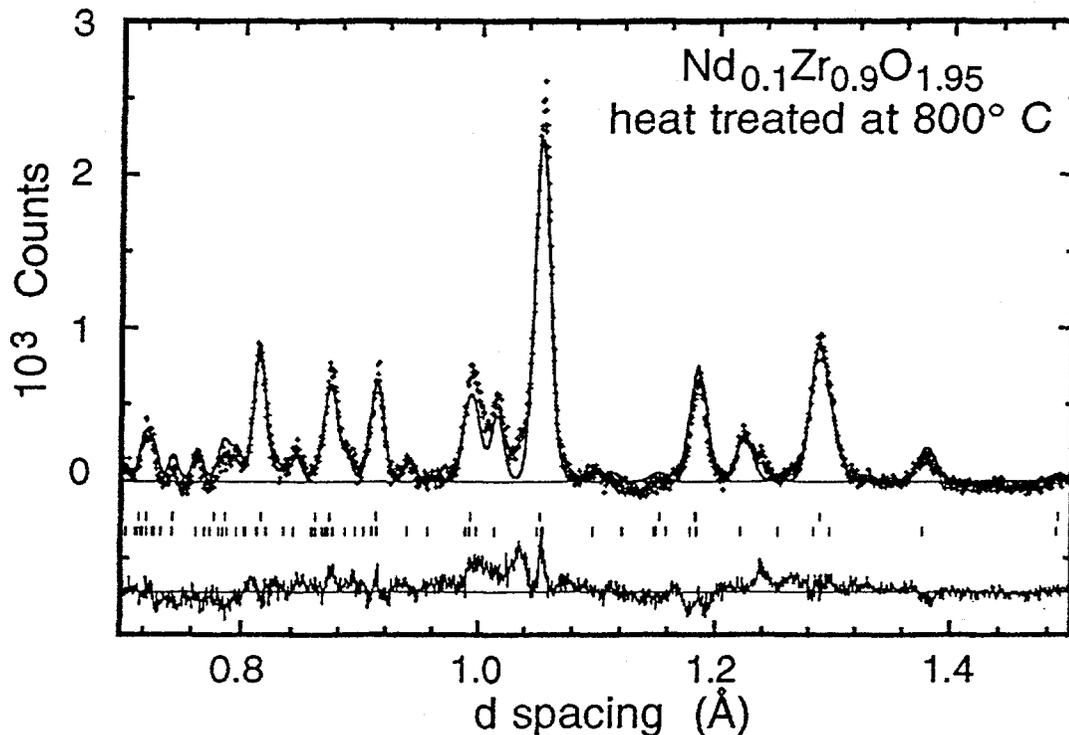


Figure 1. The Rietveld profile of Nd_{0.1}Zr_{0.9}O_{1.95}. The symbols (+) are the observed, background subtracted intensities. The solid line represents the calculated crystalline intensities. Tick marks of the top and bottom rows indicate the positions of the Bragg reflections for the cubic and tetragonal phases, respectively. The residual intensities are shown at the bottom of the figure.

the metastable phases. Second, the residual intensities show evidence of a very broad, oscillatory component characteristic of diffuse scattering from defects of short-range order. The diffuse residual intensities were analyzed by a Fourier filtering technique whereby the oscillatory component was fitted to a smooth function and then Fourier transformed into the real space, yielding a correlation function, $D(r)$. As it can be seen in Fig. 2, $D(r)$ displays four maxima at atomic spacings characteristic of short-range structure that give rise to the diffuse scattering. The first maximum at about 2.10 ± 0.03 Å corresponds to a relaxation of the Zr(RE)-O distances along the pseudocubic <111> direction. There is also evidence of additional atomic correlation at 2.66 ± 0.04 , 3.55 ± 0.04 , and 4.35 ± 0.05 Å. Similar two-phased crystal structure (weighted R-factors 4.7-6.8%) and short-range defects were also observed in La_{0.1}Zr_{0.9}O_{1.95} (heat treated to 600° C), Nd_{0.1}Zr_{0.9}O_{1.95} (heat treated at 600° C).

Fig. 3 shows the partially fitted powder pattern for the high surface-area pure ZrO_2 . Apparent in this pattern is extreme broadening of the diffraction peaks due to significant internal strain and small particle incoherency. Although the overall fit is quite poor, it seems that the pure ZrO_2 also suffers from diffuse scattering.

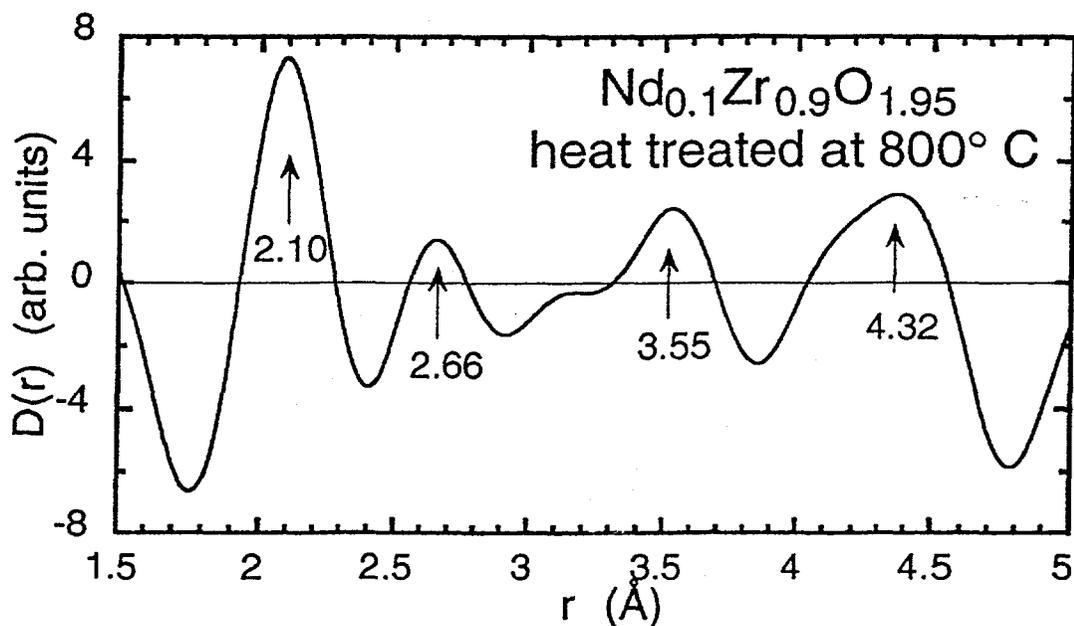


Figure 2. Correlation function, $D(r)$, calculated from the filtered residual intensities from the Rietveld refinement of the $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ data (see Fig. 1).

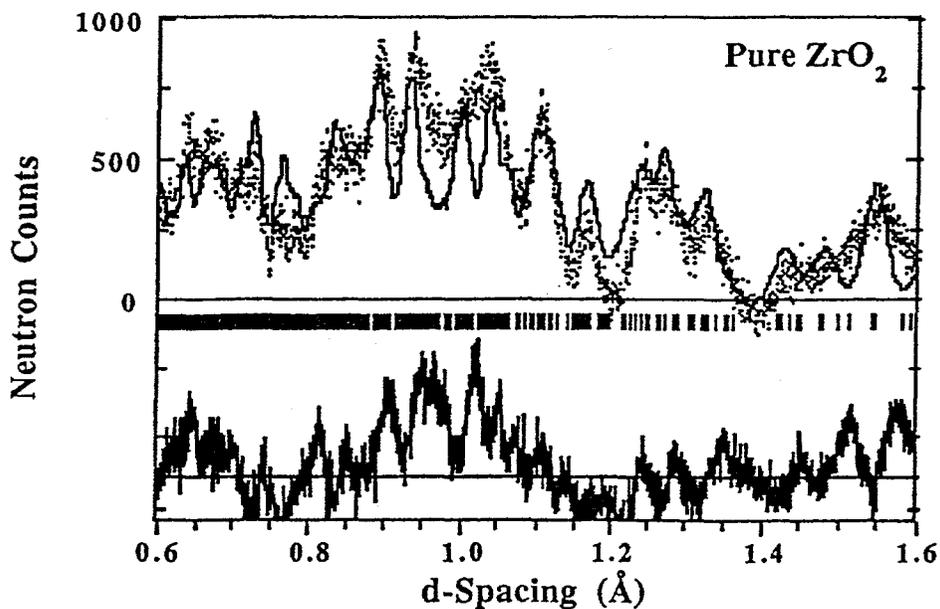


Figure 3. Rietveld profile fit for pure ZrO_2 . The broad oscillatory residual is suggestive of a diffuse scattering component, possibly due to defects.

HYDROGEN VIBRATIONAL DENSITY OF STATES OF ADSORBED WATER

Neutron inelastic-scattering experiments were performed on both the RE modified and pure ZrO_2 powders using the High-Resolution Medium-Energy Chopper Spectrometer (HRMECS) at IPNS. The measurements were conducted at 15 K and data taken at low Q ($< 10 \text{ \AA}^{-1}$) so as to minimize multiple excitations and Doppler-Shift effects. The BET-surface area determined by nitrogen adsorption at 77 K for $La_{0.1}Zr_{0.9}O_{1.95}$, $Nd_{0.1}Zr_{0.9}O_{1.95}$, and pure ZrO_2 are 78 ± 0.6 , 73 ± 0.8 , and $106.8 \pm 0.8 \text{ m}^2/\text{g}$, respectively. The RE- ZrO_2 powders were first dried by heating at 450°C in air for 4 hrs. In order to preserve the high surface area, the pure ZrO_2 powder was dried at 250°C in vacuum for 3 hrs. These dry powders contain only chemisorbed surface hydroxyl groups. Physisorbed water was then introduced by exposing the dry powders under controlled water vapor pressure inside a humidistat. The vibrational spectra of a dry $Nd_{0.1}Zr_{0.9}O_{1.95}$ powder, a 44 g $Nd_{0.1}Zr_{0.9}O_{1.95}$ with 0.33 g (low H_2O coverage) and 11.2 g (medium H_2O) of adsorbed water, and a 37.6 g $La_{0.1}Zr_{0.9}O_{1.95}$ with 1.8 g (high H_2O) of adsorbed water were studied. They are compared to the spectra of a dry pure ZrO_2 sample and a 45 g ZrO_2 with 0.58 g adsorbed water (low H_2O coverage).

The observed scattering function as a function of energy transfer, $S(E)$, for the RE- ZrO_2 are shown in Fig. 4. Since the scattering cross-section of H is more than ten times larger than those of Zr and O, the salient features in the spectra reflect mainly the hydrogen vibrational density of states of the surface hydroxyl groups and/or adsorbed water. For the dry Nd- ZrO_2 sample the weak peak at $\sim 450 \text{ meV}$ corresponds to the O-H stretch vibrations of the surface hydroxyl groups, and the broad feature below 150 meV arises from lattice vibrations. As the coverage of water increases, four bands develop: a librational band at $\sim 80 \text{ meV}$ due to intermolecular vibrations of the H_2O molecules, two intramolecular bands, one at $\sim 200 \text{ meV}$ due to O-H-O bending and the other at $\sim 430 \text{ meV}$ due to O-H stretch, and a combination band at $\sim 506 \text{ meV}$. The spectra of the dry and low H_2O coverage ZrO_2 show similar features as the correspondent RE- ZrO_2 spectra but the O-H stretch frequency for the surface hydroxyl groups shifts to a slightly higher value at 458 meV (see Fig. 6 below).

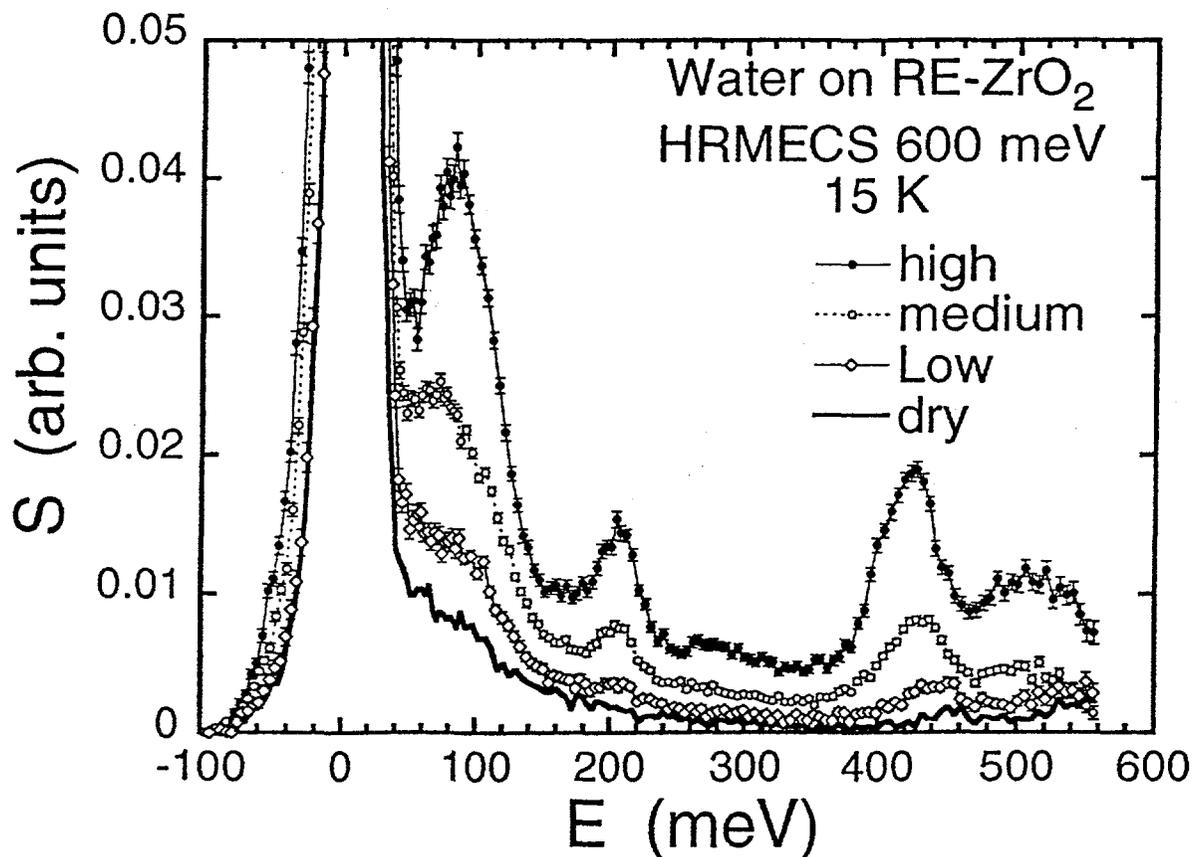


Figure 4. The observed scattering functions of water adsorbed on RE- ZrO_2 for the dry, low-, medium-, and high-water coverage (see text).

The region near the O-H stretch vibrations deserves a closer examination as it provides information regarding the competitive adhesive forces acting between the chemisorbed OH groups and the physisorbed H₂O molecules under the influence of hydrogen bonding. Electronic charge transfer processes among these molecules during a hydration process result in a change of the surface acidity. Fig. 5 shows the RE-ZrO₂ data in the 350-550 meV region fitted to a sum of multiple Gaussian functions and a linear background. In the dry Nd-ZrO₂ sample the O-H stretch band of the surface hydroxyl groups centers at 453 meV with a width (~17 meV) that is comparable to the instrumental resolution. In the submonolayer (low H₂O coverage) sample O-H stretching of the relatively isolated H₂O molecules gives rise to an additional component at 432 meV. As the coverage increases further, another component of the O-H stretch vibrations appears at 404 meV. In addition, combined H₂O libration and O-H stretch excitations result in a new, broad band at about 506 meV. In fact, the spectrum of the high water content sample resembles that of bulk water.³ In the case of the high water content sample, the two components associated with O-H stretch of the H₂O molecules sharpen slightly, probably resulted from a better organized H-bond network of the capillary-condensed water.

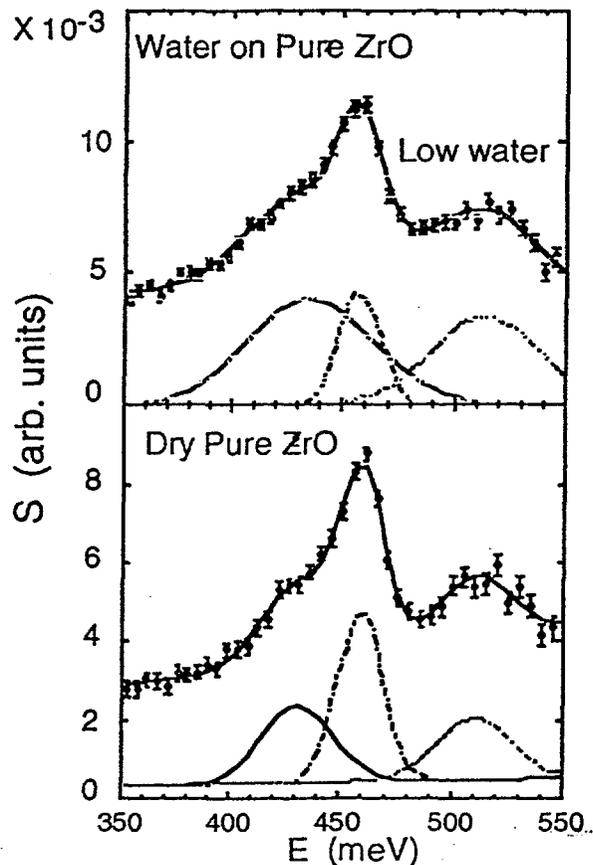
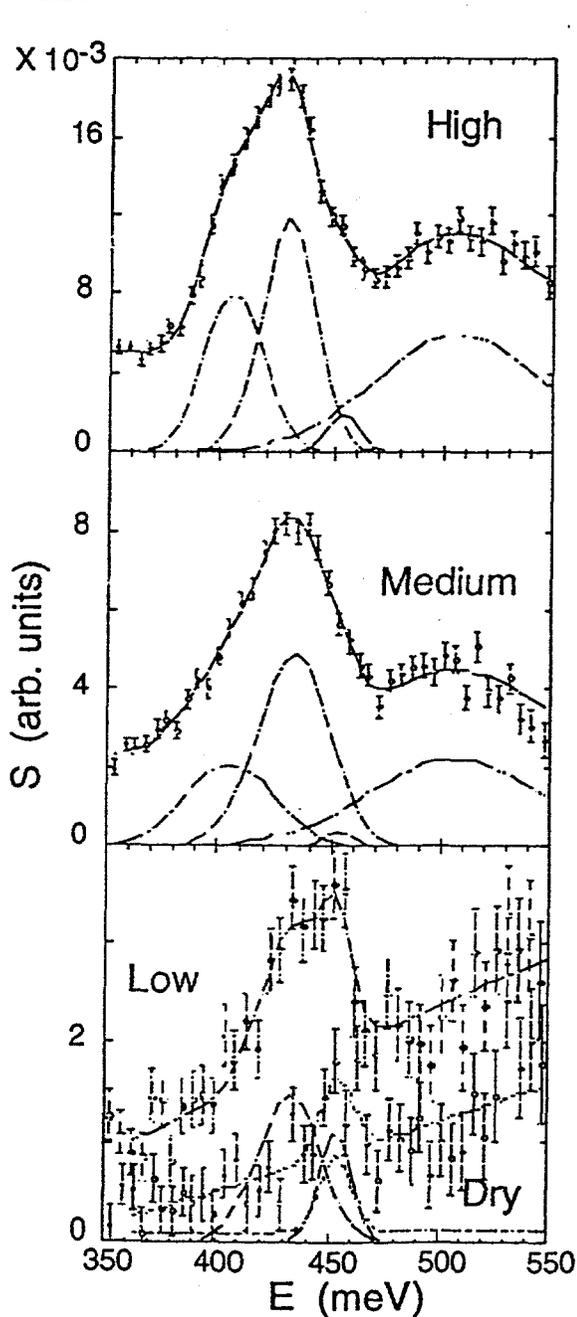


Figure 5. (left) The O-H stretch vibration band and the combination band fitted to a sum of multiple Gaussian functions and a background for the dry and low-water content samples, medium-water coverage sample, and high-water content sample.

Figure 6. (above) The O-H stretch vibrations for the dry and low-water coverage pure ZrO₂ samples.

The O-H stretch vibrations and combination band for the surface hydroxyl groups and adsorbed water (low H₂O coverage) for the pure ZrO₂ powder are shown in Fig. 6. First, the higher intensities from the dry ZrO₂ as compared to the dry RE-ZrO₂ indicate a considerable increase of chemisorbed hydroxyl groups per unit weight of the powder owing to the larger surface area in the pure ZrO₂. Second, the O-H stretch band for the hydroxyl groups occurs at ~458 meV which is somewhat higher than that for the RE-ZrO₂ powders. In addition, unlike the case of dry RE-ZrO₂, there are two broad components centered at about 432 and 510 meV. As the water coverage increases, these two components increase in intensity and broaden in width at a faster pace than the corresponding case for RE-ZrO₂ (see Fig. 5).

DISCUSSION

The diffraction and inelastic-scattering data suggest a correlation between the crystal and defects structure with the surface chemistry in RE modified and pure zirconia. For RE-ZrO₂, the average crystal structure is partially stabilized to a major tetragonal and a minor cubic phase with the presence of a small, short-range defects component. The crystal structure of a pure ZrO₂ powder, on the other hand, is monoclinic, and shows no evidence of additional defects component. The spectrum of dry RE-ZrO₂ exhibits a peak at about 453 meV characteristic of the O-H stretch vibrations of surface hydroxyl groups whereas the corresponding peak for dry pure ZrO₂ occurs at about 458 meV. During the hydration process in both RE-ZrO₂ and pure ZrO₂, three additional bands corresponding to the O-H stretch (~432 meV), H-O-H bend (~200 meV) and librational motion (~80 meV) were observed. The somewhat decreasing energy and increasing width of the O-H stretch band with increasing H₂O coverage indicate the influence of hydrogen bonding on the motion of water molecules.

Although the formation of surface hydroxyl groups and the water adsorption on RE-ZrO₂ and ZrO₂ depend on the method of synthesis, our structural data for RE-ZrO₂ are consistent with those in previous studies of yttria-stabilized ZrO₂ by various workers.⁴⁻⁸ The vibrational spectra of the pure ZrO₂ covered by surface hydroxyl groups and adsorbed water also agree qualitatively with those observed in a low surface-area zirconia sample by Tret'yakov and co-workers using infrared spectroscopy.⁹ Obviously, more investigations such as absorption isotherm of water on the present samples are needed to further clarify the nature of the hydration process in zirconias.

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