I. INTRODUCTION

Nanomaterials have aroused great interest because of their unusual properties resulting from peculiar microstructure of nanograins, their basic construction units.\(^1\) When the average grain size is controlled in the range of 1–100 nm, their physical and chemical properties can be significantly different from those of bulk materials owing to space confinement and surface effects.\(^3\)\(^,\)\(^4\) It is important to understand the manner in which the structures and properties of a single nanograin vary with grain size, from atomic behavior to bulk solid-state behavior. Nanomaterials synthesized by different methods could have different microstructures such as nanocrystallite, nanoamorphous grain, or nanoclusters assembles with some crystal feature, which underlie their physical and chemical properties. It is essential to study the relationship of internal microstructure of nanograins with grain size for understanding physical mechanisms involved in nanomaterials and cooperative atomic phenomena such as lattice vibration.

The size of nanograins can be controlled by annealing nanomaterials. Their structures and the approximate mean size are conventionally determined by x-ray diffraction (XRD). A few papers have recently reported detailed XRD studies of the lattice distortion in nanomaterials and the microstructure changes with annealing temperature.\(^5\)\(^,\)\(^6\) The vibrational properties of nanomaterials, which are strongly dependent on the nanograin size, are usually studied by Raman spectroscopy, which is a powerful characterization technique concerning molecular vibrations and dynamical properties of materials. We intend to combine these techniques and correlate their results.

Zirconium oxide (ZrO\(_2\)) is a useful functional material in high-temperature optical and electronic technologies,\(^7\) and is also a typical material in structural-phase transitions because ZrO\(_2\) can exist in several polymorphs.\(^8\) There is a lot of work performed using IR\(^9\)\(^,\)\(^10\) and Raman\(^8\)\(^,\)\(^11\) techniques to characterize the structures and properties of ZrO\(_2\). In this paper, x-ray spectroscopy in range $\theta = 10^\circ-80^\circ$ and Raman spectra over a large frequency range 80–1250 cm\(^{-1}\) are measured systematically for ZrO\(_2\) nanograins of the size ranging from 5 nm to 1 \(\mu\)m at room temperature. Compared with previous papers,\(^12\)\(^,\)\(^13\) our results are improved and complete in the sense that additional vibrational modes of nano-ZrO\(_2\) can be resolved together with a characteristic mode around 1050 cm\(^{-1}\) (a surface vibrational mode). These results provide useful information for studying the relationship between the grain size, the microstructure of nanograins and their vibrations.

II. EXPERIMENT

ZrO\(_2\) nanograins of average diameter $\sim 5$ nm were prepared using the hydrothermal method from a solution of 1N zirconium nitrate in 2N nitric acids (N for normality concentration) after heating to 150 °C for 12 h in a sealed hyperbaric vessel cushioned with polytetrafluoroethylene, and then cooled to room temperature. White ZrO\(_2\) powder was obtained after washing the product alternately and repeatedly with water and absolute acetone, which was dried in a vacuum desiccate for 14 h. ZrO\(_2\) nanograins of different size were obtained by annealing the powder at different temperatures for 8 h. A series of annealing temperatures were chosen: 200 °C, 300 °C, 450 °C, 500 °C, 800 °C, and 1100 °C. The powders were compressed under 10 GPa into circular pieces of diameter $\sim 10$ mm and thickness $\sim 1$ mm.

An x-ray diffractometer (Rigaku D/Max-r) was used for structure identification with Cu K\(\alpha\) radiation. The operating voltage and current were 50 kV and 200 mA, respectively. A transmission electron microscope (TEM, Hitachi 900) was...
used to take feature micrographs. The average size of ZrO$_2$ nanograins was determined by XRD and TEM. Two Raman spectrometers were used for investigating the vibrational modes of ZrO$_2$ nanograins at room temperature. One was a SPEX-1403 Ramalog system together with an argon ion laser (Coherent Innova-100), which provided 514.5- and 488.0-nm lines for excitation. Another was a Bruker 100 system, a near infrared (NIR) Fourier transform (FT) Raman spectrometer with a cw diode-pumped Nd:YIG (yttrium indium-garnet) laser for 1.06-μm excitation and with a liquid-nitrogen-cooled germanium detector. Backscattering geometry is adopted for all Raman measurements. In general, Raman spectra were collected under the conditions of laser power 50 mw and resolution 4 cm$^{-1}$. Typically 2500 scans at 4 cm$^{-1}$ interval were averaged to provide a spectrum of sufficient quality. Results from two spectrometers are similar and only the NIR-FT Raman results are shown.

III. RESULTS AND DISCUSSION

Figure 1 is the XRD spectra of nano-ZrO$_2$ with different annealing temperatures $T_a$: n1, as-grown sample; $T_a=200$, 300, 450, 500, 800, and 1000 °C, respectively, from n2 to n7.

The increase in grain size as $T_a<500$ °C is moderate, which manifests that low-temperature annealing mainly removes the interface stress and effects the interface-structure relaxation. After 500 °C the grain size increases rapidly when annealing mainly causes grain growth.

From n1 to n7 the grain size increases and correspondingly their XRD peaks are sharpening and resolving into fine structure. The as-grown sample n1 has eight broad diffraction peaks situated in the similar ranges of the monoclinic polycrystalline ZrO$_2$ spectrum. However, the bandwidths are large (so that the resolution is low), the positions shift, and the relative intensities are different from the literature data. It is a deteriorated bulk spectrum, which is closely related to the fact that the presence of large numbers of lattice vacancies and local lattice disorders may result in considerable reduction in intensity and even lead to near disappearance of XRD peaks of crystal planes. The as-grown nanograins possess maximum structure disorders: oxygen vacancies, local lattice disorder, cluster pores, and etc. The smallest grain size also means the largest grain surface. There are huge numbers of interfaces between and inside nanograins so that many atoms or molecules of nanograins are in the surface or near-surface states. Therefore the n1 spectrum is the least bulk-like. There is no drastic change in the positions and intensities of XRD peaks from n2 to n5, although a tendency towards stronger peaks is apparent. It is consistent to the explanation that annealing under $T_a<500$ °C is able to re-

![FIG. 1. XRD spectra of nano-ZrO$_2$ with different annealing temperature $T_a$: n1, as-grown sample; $T_a=200$, 300, 450, 500, 800, and 1000 °C, respectively, from n2 to n7.](image)

![FIG. 2. Raman spectra of nano-ZrO$_2$ with different annealing temperatures (n1–n7).](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>n1</th>
<th>n2</th>
<th>n3</th>
<th>n4</th>
<th>n5</th>
<th>n6</th>
<th>n7</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_a$ (°C)</td>
<td>as-grown</td>
<td>200</td>
<td>300</td>
<td>450</td>
<td>500</td>
<td>800</td>
<td>1100</td>
</tr>
<tr>
<td>D (mm)</td>
<td>5.0</td>
<td>8.0</td>
<td>12</td>
<td>15</td>
<td>20</td>
<td>75</td>
<td>120</td>
</tr>
</tbody>
</table>

TABLE I. The average grain sizes of nano-ZrO$_2$ annealed under different temperature.
move stress and lead to relaxation in the interface structure, but is difficult to eliminate local lattice disorders or to change the internal structure of nanograins owing to their requirement for higher energy. The spectra of n6 and n7 are much bulklike, qualitatively different from the previous ones. The diffraction peaks sharpen, strengthen, and can be indexed according to the standard monoclinic structure. It shows that the grains have improved greatly. The rapid increase in grain size as $T_a \geq 500$ °C is accompanied with a rapid decrease in the density of vacancies, local lattice disorders, and clusters pores.

Bulk ZrO$_2$ is monoclinic, belonging to the space group $C_{2h}^5 (P2_1/c)$. A unit cell contains four formulas. Its vibration properties have been investigated. According to group theory, there are 36 lattice vibrational modes:

$$G_{\text{mono}} = 9A_g + 9A_u + 9B_g + 9B_u$$

among which $9A_g$ and $9B_g$ modes are Raman active, while $8A_u$ and $7B_u$ modes are infrared active and others are acoustic modes.

The NIR-FT Raman spectra of nano-ZrO$_2$ with grain size ranging from 5 to 120 nm ($n1$–$n7$) are shown in Fig. 2, which are similar using 514.5 and 488.0 nm beam for excitation. To compare with published data, Table II lists the Raman frequencies of nano-ZrO$_2$ together with the frequencies of the ZrO$_2$ modes given in other sources. For the sample $n7$ annealed at 1100 °C (the grain size is larger than 120 nm), our results are similar to Refs. 8 and 11 and can be interpreted based on the single-crystal or polycrystalline spectrum. There is no vibrational mode at 148 cm$^{-1}$ or 266 cm$^{-1}$ in any sample, which are attributed to the tetragonal phase. The n6 spectrum is similar to n7 but the spectra from n1 to n5 are deteriorated bulk spectra with new features. These results indicate that the samples are basically single-phase ZrO$_2$ of monoclinic structure, in good agreement with XRD.

In Fig. 2, the Raman modes display usual anharmonic effects as the grain size decreases. Broadening, peak merging, and frequency shifting are observed. There are also some new features in the spectra. For example, an additional Raman mode, denoted as $S$, at 1038 cm$^{-1}$ appears in the spectra of samples $n1$ to $n5$ as the grain size is under 20 nm, which has asymmetric broadening on the low-frequency side of the peak. $S$ strengthens and shifts toward higher frequency (1050 cm$^{-1}$) as the grain size decreases. Furthermore, 15 weak modes are observed in the sample n1 of grain size 5 nm.

It is noteworthy that the Raman spectra of nano-ZrO$_2$ vary systematically with grain size in the mode position, line-width, and intensity. Their general behavior divides into three categories: Group C includes lines in the region 100–700 cm$^{-1}$; line S varies in the range 1030–1050 cm$^{-1}$; and Group H concerns the weak features in the region 700–1250 cm$^{-1}$. The spectral lines in Group C strengthen and resolve into sharp peaks with increase of grain size, following the evolution tendency of the XRD spectra. On the contrary, the line $S$ and Group $H$ behave oppositely and the Group $H$ is very weak.
The sample $n7$ has a bulk vibrational spectrum of monoclinic ZrO$_2$ crystal. The spectrum deteriorates continuously from $n6$ to $n1$, in the region of Group $C$. Each mode is denoted by its wave number as subscript. Their Raman shifts are listed in Table II where each row shows the variation of a mode frequency with grain size. The tendency of frequency shifting is clearly shown by Fig. 3, a graph of mode frequency versus annealing temperatures where each row of Table II becomes a line. The frequency variation is usually several cm$^{-1}$ and red shift with grain-size reduction is common but blue shift also occurs. As grains contract, lines broaden and some merge with each other. In the meantime, the relative intensities of Raman modes also change. For example, the $A_g$ modes $C_{178}$ and $C_{191}$ of $n7$ attenuate about twofold towards $n1$ and merge into a broad peak $C_{178}$ of $n1$. $C_{178}$ is stationary but $C_{191}$ shifts to 178 cm$^{-1}$ of $n1$, with a redshift as large as 13 cm$^{-1}$. Its FWHM almost doubles. Another example is the $A_g$ mode $C_{475}$ of $n7$, the strongest in the spectrum, which weakens to being similar to others towards $n1$. We conclude that Group $C$ concerns bulk phonons and manifests the persistence of the basic polar-mode properties of the single crystal in nanograin.

The behavior of Group $C$ shows clearly the dependence of Raman scattering by polar modes in a collection of randomly oriented crystallites on the size of the individual crystallites, as summarized in the Chapter 4 of Ref. 16. Similar behavior appears in LiIO$_3$ powder. Gualberto and Argüello obtained a good agreement between the experimental results and theoretical calculation of the spectral differential cross section of LiIO$_3$ powder.\cite{17} Otaguro \textit{et al.} studied the orientation dependence of the single-crystal polar-mode frequencies of LiIO$_3$ in the similar frequency range.\cite{18} The details of the powder spectra are quite different from the single-crystal spectrum: not all the single-crystal peaks appear in the powder spectra and some that do appear are displaced in frequency and changed in intensity. The powder ones shows a continuous distribution over the range of the single-crystal polar-mode frequencies. Systematic change in grain size makes the tendency in spectral change clear.

The mode $S_{1050}$ is the characteristic of $n1$. Single-crystal or polycrystalline ZrO$_2$ does not have any $S$ mode, which appears only in ZrO$_2$ nanograins of small grain size ($\leq 15$ nm). Figure 2 shows that the intensity of $S$ drops as nanograins grow. $S$ disappears completely when grain size reaches 50 nm. The grain-size dependence of the $S$ intensity relative to that of $C_{475}$ of $n1$ is shown in Fig. 4. The ratio of the number of superficial atoms $N_S$ to the total number of atoms $N_T$ versus grain size following Ref. 19 is plotted in the inset. Both increase rapidly when particle size decreases below 15 nm, suggesting some inner link. However, they have different coordinates scale (relative intensity and percentage) and $I_{S_{1050}}/I_{C_{475}}$ has a dramatic drop for a diameter larger than 15 nm but the ratio $N_S/N_T$ is a smoothly and slowly varying function, which make them dissimilar. It would not be possible to draw causal relation from comparison between two. On the other hand, this behavior is similar to the Raman spectra of small particles of silicon.\cite{20} $S$ mode behaves similarly to the Raman-scattering cross section of surface phonon in very small GaP spherical crystals calculated by Ruppin.\cite{21} As the bulk-mode transverse and longitudinal cross sections of GaP sphere keep almost the same when sphere size changes, the surface-mode cross section exceeds them for sphere diameter smaller than about 20 nm, becomes comparable with the bulk-mode scattering for sphere diameter $\sim 100$ nm and drops dramatically to being negligible for diameter $>200$ nm. The predominance of the surface-mode scattering at extremely small size in the order of magnitude of sphere diameter $\sim 20$ nm is the most striking modification of the spectral results. The basic reason why the powdered specimen show new spectral features is that the wave-vector...
conservation condition no longer limits the modes that contribute to light scattering when the particle size \( D \) is so small that \( Dq \approx 1 \), where \( hq \) is the momentum transferred.\textsuperscript{16,18} For visible incident light of a typical wavelength \( \sim 514 \text{ nm} \) (the green light of \( \text{Ar}^+ \) laser) into a crystal of refractive index \( \sim 1.5 \), its wave vector \( \sim 1.8 \times 10^7 \text{ m}^{-1} \) so that the maximum \( q \approx 3.6 \times 10^7 \text{ m}^{-1} \) (Ref. 16) and \( D \) would be smaller than \( \sim 30 \text{ nm} \). Hayes and Loudon,\textsuperscript{16} however, pointed out that the scattering is nevertheless difficult to observe, and the crystallite in real powders are not usually spherical or even ellipsoidal, but have irregularities that broaden the surface-mode peak. Systematic reduction in size of nano-ZrO\(_2\) provides an opportunity to observe the emerging and development of the surface-mode peak. We attribute \( S \) mode to surface-mode scattering, which is another observed surface phonon in addition to one from scattering by CdS crystallites.\textsuperscript{22}

Figure 2 also shows that the mode \( S \) blueshifts from 1040 \( \text{ cm}^{-1} \) (\( n4 \)) to 1050 \( \text{ cm}^{-1} \) (\( n1 \)). It seems to be tempting to attribute this blue shift to quantum-size-effect related mechanism such as the surface electron-phonon interaction. A nanocrystal exciton model has been used to explain the blue shift of the absorption edge in photoacoustic spectrum and the absorption peaks of first-order differential PAS of nano-ZrO\(_2\).\textsuperscript{5} which was used in previous Raman-scattering work, too.\textsuperscript{12} However, this interpretation of the blueshift of mode \( S \) is not convincing. By the spheroid model of nanoclusters, the energy of the exciton ground state of nano ZrO\(_2\) can be expressed as \textsuperscript{23}

\[
E = E_g + \frac{\hbar^2 \pi^2}{2R^2} \left( \frac{1}{m_e} + \frac{1}{m_h} \right) - 1.786 \frac{e^2}{\varepsilon R} - 0.248E_{\text{Ry}},
\]

where \( R \) is the radius, \( \varepsilon \) is the dielectric constant, \( m_e \) and \( m_h \) are the effective masses of the electron and the hole, respectively, and \( E_{\text{Ry}} \) is the effective Rydberg energy. On the right-hand side, the first term is the energy gap, the second is the quantum-size energy of localization, the third is the Coulomb interaction energy, and fourth results from the spatial correlation effect. The first term is constant and the fourth is independent of the size and usually small. The second \( (\sim 1/R^2) \) and third \( (\sim 1/R) \), respectively, represent an increase and a decrease in energy and are mutually canceling. The quantum size energy of localization will prevail as grain size decreases. When it dominates over the Coulomb energy, the excitation energy increases and could be higher than that of the eigenstate, which results in a blueshift of the peak. However, why should the energy of surface vibrations be related to the energy of an exciton? More relevant interpretation should relate the blue shift of surface vibration to surface itself. It results likely from surface relaxation as the particle size decreases. A surface optic phonon was observed on the TaC(100) surface by inelastic electron scattering\textsuperscript{24} and for TaC with simple rocksalt crystal structure the dispersion curve of the surface mode on (100) can be calculated applying the diatomic linear-chain model.\textsuperscript{25} The theoretical dispersion values based on this nearest-neighbor central-interaction model are smaller than the experimental ones because of modified force constants (surface relaxation) near the surface or owing to the effect of second- and third-neighbor forces. Although there is no simple theoretical model for the surface mode of monoclinic ZrO\(_2\), similar change in force constants might occur owing to surface relaxation, which strengthens as the particle size decreases. Corresponding increase in force constants causes the blueshift.

Group \( H \) includes weak features at 704, 714, 725, 807, 835, 859, 874, 911, 928, 938, 955, 1145, 1167, and 1224 \( \text{ cm}^{-1} \), clearly observable in Fig. 5. They are sharp with Lorentzian line shape and linewidth in the region 10–20 \( \text{ cm}^{-1} \). Their frequencies are too high to be related to the first-order silent modes. They are likely the second-order active Raman modes. A Raman or infrared spectrum of a crystal (molecule) may contain numerous combination and overtone bands arising from anharmonicity. An ideal crystal has infinite spatial correlation length of phonon, and hence, the phonon eigenstates are plane wave. It leads to the usual selection rule, phonon momentum \( q \not\equiv 0 \) for the first-order (the upper limit of \( q \) is three orders of magnitude smaller than the Brillouin-zone boundary) and \( q + q' = 0 \) for the second-order two-phonon (now phonon wave vectors \( q \) and \( q' \) are typically three orders of magnitude larger than the light wave vectors over the major part of the Brillouin zone) Raman scattering. The order of a real crystal, however, is not perfect owing to defects, impurities, disorder, etc. It means that the spatial correlation function of the phonon becomes finite in extent. It relaxes the selection rule, which, in turn, results in observation of symmetry-forbidden modes, together with line broadening and asymmetry of line shape, as well as redshifting of phonon mode. A combination band belongs to the direct product of representations to which the internal fundamental vibrations belong and its observed frequency is
the sum of their frequencies.\textsuperscript{26} For overtone bands, the characters of vibration representations are given by\textsuperscript{27,28}

\[ \chi_{\nu R}(R) = [\chi_{\nu}(R)]^2, \quad \text{for } f = 1, \]

\[ \chi_{\nu f}(R) = (1/2) \{[\chi_{\nu}(R)]^2 + \chi_{\nu}(R^2)\}, \quad \text{for } f \geq 2, \]

where \( \chi_{\nu}(R) \) is the character under the operation \( R \) for the \( f \)-fold degenerate irreducible representation \( \nu \) of the point group, and \( \chi_{\nu f}(R) \) is the character of the reducible representation of the first-order overtone whose fundamental vibrations belong to \( f \)-fold degenerate \( \nu \). These bands have well-defined frequencies and widths in the same order of magnitude as the fundamental bands. In these cases, predictions from selection rules based on the factor group are generally sufficient.\textsuperscript{26,29} Higher-order Raman modes are usually very weak, e.g., the intensity of second-order Raman modes is about one or two orders of magnitude smaller than that of their fundamental modes. Figure 2 gives the ratio of intensities \( I_{478}/I_{550} = 22 \). The higher-order Raman modes in \( n \) are listed in Table III, in good agreement with quantum theory. The appearance of high-order modes in Raman spectra of nano-ZrO\(_2\) brings new possibility for studying the microstructures of nanograins because the selection rules of high-order modes are different from those of fundamental modes.

In summary, sample \( n \) distinguishes between the samples that show notable “size + interface” effects and the samples in which bulk properties predominate. Its surface mode \( S \) and Group \( H \) almost disappear and its bulk phonon modes start to intensify, showing reduction of the lattice vacancies and local lattice disorder. Correspondingly, its lattice distortion weakens and all XRD peaks start to strengthen. Nanograin samples show bulklike spectra as \( D > 15 \) nm, which manifests grain growth improves crystallite quality. Samples of \( D \lesssim 15 \) nm, on the contrary, show deteriorated bulk spectra with clear “finger print” of size and interface effects.

IV. CONCLUSIONS

We have systematically measured XRD and Raman spectra of ZrO\(_2\) nanograins of size in the region 5–120 nm at room temperature. Both the structure and vibration of nanograins of size under 15 nm show characteristics different from bulk ones. Their essentially monoclinic bulk properties diminish. Their spectral-line weakens, broadens, and merges. In Raman spectra shifts of modes are common, an extra surface vibrational mode \( S \) around 1040 cm\(^{-1}\) and weak second-order Raman modes (Group \( H \)) appear. The results show the effects of defects, size and interfaces in typical ZrO\(_2\) nanograins. On the other hand, nanograins of size above 20 nm are very similar to bulk solids. The bulk characteristics recover in both spectra, showing the predominance of interior order. It suggests that the modes \( S \) and Group \( H \) are closely related to the change of nanograin microstructure.

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