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Trapping of cubic ZnO nanocrystallites at ambient conditions

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Abstract

Dense powder of nanocrystalline ZnO has been recovered at ambient conditions in the metastable cubic structure after a heat treatment at high-pressure (15 GPa and 550 K). Combined x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) experiments have been performed to probe both long-range order and local crystallographic structure of the recovered sample. Within uncertainty of these techniques (about 5%), all the crystallites are found to adopt the NaCl structure. From the analysis of XRD and XAS spectra, the cell volume per chemical formula unit is found to be 19.57(1) $\AA^3$ and 19.60(3) $\AA^3$, respectively, in very good agreement with the zero-pressure extrapolation of previously published high-pressure data.

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With a direct band gap of 3.4 eV at ambient conditions, wurtzitic ZnO (w-ZnO), like GaN or 6H-SiC, is intensively studied in view of potential applicability in the field of opto-electronics (*e.g.* laser or light-emitting diodes) [1]. Furthermore, in comparison with its previous competitors, w-ZnO combines several unique electrical, acoustic and chemical properties which make it one of the most technologically relevant binary compounds [2].

Recently, it has been shown that intentionally as well as unintentionally doped w-ZnO give rise to high-quality n-type (electron) conductivity that directly comes with its wurtzite ambient condition stable structure [3]. The p-type w-ZnO conductivity has been theoretically predicted to be increased by doping with nitrogen through the use of NO or NO_2 [4] and some recent publications demonstrated that p-type w-ZnO thin films could be fabricated [5–7]. However, physical limitations preclude the synthesis of high p-type (hole) conductivity, and therefore, the practical applicability of novel short-wavelength optoelectronic devices based on p-n junctions [8]. On the other hand, ZnO in its ionic NaCl high pressure phase (c-ZnO) has an electronic structure with an indirect band gap that may be compatible for high p-type doping. The possibility to trap this high pressure phase at ambient condition would therefore be of great interest. Several high pressure structural investigations of ZnO have been done in the last two decades [9] and all agree that the w-ZnO $\mapsto$ c-ZnO transition is reversible at ambient temperature (with a transition pressure of 9 GPa upon increasing pressure and 2 GPa upon decreasing pressure [10]). In this work, we demonstrate a way to obtain c-ZnO crystallites metastable at ambient conditions based on the peculiar physical features observed in the nanocrystal regime.

Unlike extended solids, nanocrystals are nearly interior defect-free and externally faceted with a defined shape directly related to the crystallographic structure. Under pressure, a structural transformation in these systems occurs with a single nucleation center per crystallite [11] which is usually associated with a shape change [12, 13]. Thus, the average surface tension as well as the surface areas of the nanocrystallites should obviously affect the internal energy difference between the high and low pressure structure, unlike bulk crystals. For example, measurements on CdSe [11] indicate that both forward and backward pressure transition are particle-size dependents. In a same manner, Jiang [14] found an enhancement of the upstroke transition pressure (15.1 GPa) in 12(2) nm size ZnO nanocrystals compared to the bulk value. After a decompression from 52.5 GPa down to ambient pressure, a coexistence of the $w-$ and $c-$phases was recovered with a large fraction of NaCl phase. We

reproduced this experiment with the same type of nanopowder (12(2) nm) and we found that the $c-$fraction of recovered sample after decompression at ambient conditions increases with the maximum pressure reached upon compression. This phenomenon can not be ascribed to a size distribution effect, since above the transition pressure the whole sample is observed to be in the high pressure phase independently of the maximum pressure reached (which also rejects a possible effect due to a pressure gradient). From the work of Tolbert[11] and Wickham[13], we suggest that this phenomenon is related to the shape change of the crystallites which occurs at the phase transition. At room temperature, and pressure above the phase transition, a fraction of the crystallites may acquire an unstable shape compared to the equilibrium configuration one (despite the interior high-pressure structure). Since the shape change (due to atomic diffusion) is mainly determined by a dynamic processes, heating at high pressure should help to anneal the unstable shape to the equilibrium one. Finally, heating would lead to a larger number of rocksalt nanocrystallites of ZnO trapping at ambient conditions.

Obtained from planetary ball mill, nanocrystalline powder of w-ZnO with average size of 12(2) nm was used in this work. The high pressure cell was a membrane diamond anvil cell (DAC) specifically designed for high temperature studies [15]. The DAC was surrounded by a heater and a thermocouple was glued on one end of the diamond anvil to determine the average temperature on the sample with an accuracy of 20 K. A rhenium gasket was preindented from 200 to 30 μm, and a 150 μm hole was drilled in the center by spark-erosion. Silicon-oil was used as a pressure transmitting medium because it is amorphous and chemically inert. Pressure was measured using the fluorescence emission of a ruby ball [16] placed into the gasket hole. The accuracy was better than 1 GPa at the maximum pressure reached.

Combined x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS) experiments have been performed at the LURE synchrotron facility in Orsay (France), giving respectively long-range and local structure. The powder x-ray diffraction measurements were made in the energy dispersive mode with the wiggler at DW11 station. After the energy calibration of the Ge detector, the 2θ angle was determined by collecting diffraction patterns of a gold sample placed in between the anvils. The polychromatic x-ray beam was collimated to a 50×50 μm^2 spot centered on to the gasket hole. Absorption spectroscopy was performed at the D11 dispersive XAS station at the Zn K edge (see reference [17] for technical details)

and the Zn-O distance was deduced from the experimental data using the FEFF6 [18] codes for theoretical calculations of x-ray absorption fine structure including multiple-scattering pathways.

The sample was first pressurized at ambient temperature up to 15 GPa and then heated to 550 K. Under these conditions, ZnO was in a pure rocksalt structure ($Fm3m$) as expected from the phase diagram of the extended crystal [19]. After cooling down to 300 K and a gradual decompression to ambient pressure, the crystallographic structure of the sample recovered from the previous P-T path was examined in detail by XRD and XAS.

X-ray diffraction spectra recorded before and after high-pressure treatment are reproduced in fig. 1. Exposure times between 30 and 40 min were sufficient to collect diffraction patterns with suitable signal to noise ratio. The five peaks observed in the recovered sample spectrum are unambiguously indexed to a cubic cell and used to compute the structural parameter, leading to a_0=4.278(3) $\mathring{A}$ (*i.e.* V_0=19.57(1) $\mathring{A}^3$).

The local structure (up to 8 $\mathring{A}$) around the Zn atoms of ZnO has been probed by XAS. X-ray absorption fine structure (XAFS) spectra before and after high-pressure high-temperature cycle are compared in fig. 2 with that of pure rocksalt zinc oxide recorded at 15 GPa and 300 K (after cooling down from 550 K). Here again, the recovered sample is found to be in a sixfold coordination scheme (within uncertainty of 5%, given by the crystalline structure sensitivity of both XRD and XAS techniques) corresponding to a NaCl type structure (in $w-$ZnO, the coordination number is four).

Figure 3 shows the magnitude of the experimental and calculated Fourier transform. The theoretical data have been fitted for a cubic structure to the experimental spectra in the [0.5-3.65 $\mathring{A}$] range with only four parameters: the first-neighbor distance d_{Zn-O}, the corresponding variance σ^2, the theoretical energy origin E_0 and a nonstructural parameter S_0^2 for amplitude correction. The best fit gives d_{Zn-O}=2.14(1) $\mathring{A}$ (*i.e.* V_0=19.60(3) $\mathring{A}^3$), in very good agreement with the present XRD data, as well as with the zero-pressure extrapolation of high pressure x-ray diffraction data obtained on bulk cubic ZnO: V_0=19.66 $\mathring{A}^3$ [19], V_0=19.48 $\mathring{A}^3$ [20] or V_0=19.60 $\mathring{A}^3$ [9].

In conclusion, while the wurtzite-to-rocksalt phase transition has been shown to be reversible for bulk ZnO crystals, this property is demonstrated to be drastically altered by the reduction of grain size. From the combined XRD and XAS observations, we argue that high-pressure (15 GPa) heat (550 K) treatment of ZnO nanocrystallites yields to a single

metastable cubic phase of zinc oxide at room conditions. This result is of most interest since this metastable phase may open a broad range of new technical applications as heterojunctions for photodetection and photovoltaic devices [21]. Moreover, while a small volume of $c-$ZnO powder has only been obtained in the present work (through the use of diamond-anvil cell), the $P-T$ conditions required to obtain this sample can also be reached by multi-anvil high-pressure apparatus where the sample volume is of 100 mm^3. Finally, and from a more general point of view, the present study indicates that the phase diagram of semiconductors with reduced size may be different from that of the bulk compounds and deserve new studies.

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Figure caption

Figure 1:

X-ray energy dispersive spectra for nanopowder of ZnO at ambient conditions before (bottom pattern) and after (top pattern) the high-pressure high-temperature (15 GPa, 550 K) cycle. A single NaCl phase spectrum of ZnO measured at 10 GPa and 1000 K (V=19.16 $\mathring{A}^3$) is also shown for comparison.

Figure 2:

Zn K-edge XAFS $k\chi(k)$ experimental data for nanopowder of ZnO before (bottom pattern) and after (top pattern) high-pressure high-temperature (15 GPa, 550 K) cycle, compared with the experimental kχ(k) signal of pure $c-$ZnO recorded at 15 GPa and 300 K.

Figure 3:

Magnitude of the Fourier transform of the recovered sample $k^2\chi(k)$ spectra (solid line) compared with the best fit of theory (dotted line) including all single and multiple-scattering paths between 0.5 and 3.65 $\mathring{A}$. The best fit is obtained with d_{Zn-O}=2.14(1) $\mathring{A}$, σ^2=0.01 $\mathring{A}^2$, E_0=9659.4 eV and S_0^2=0.83.

Figures

Figure 1

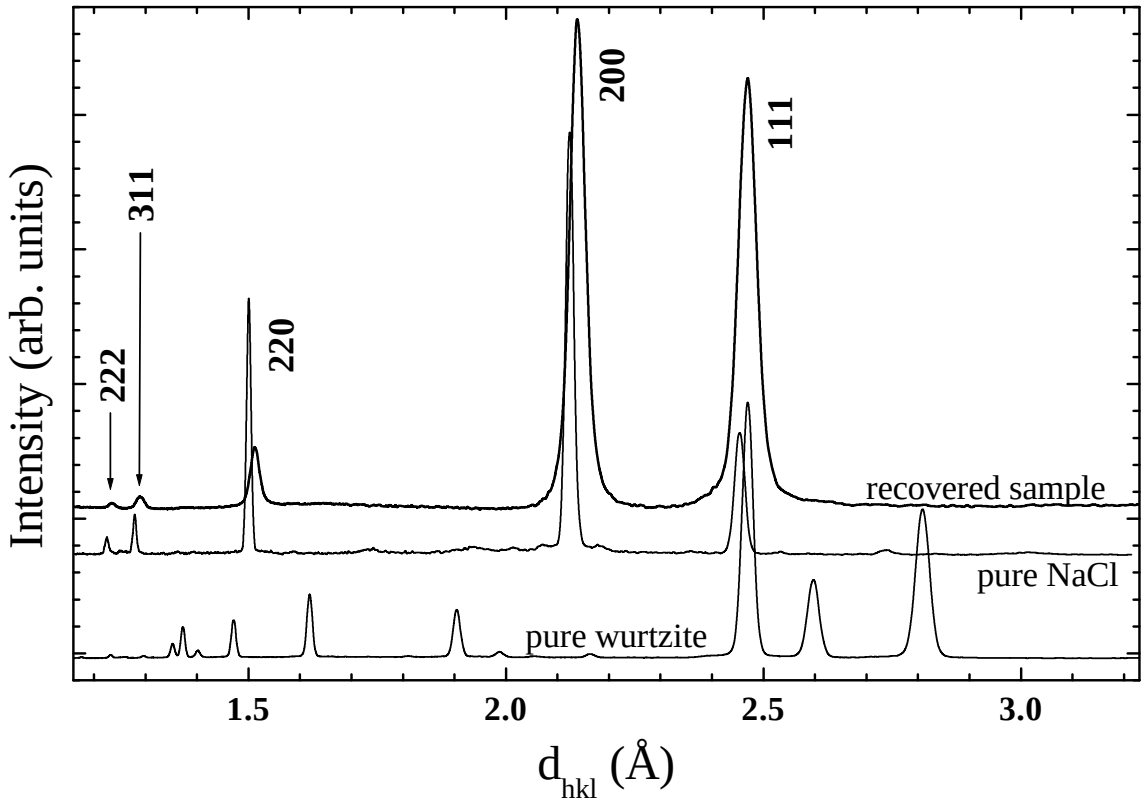

FIG. 1:

Figure 2

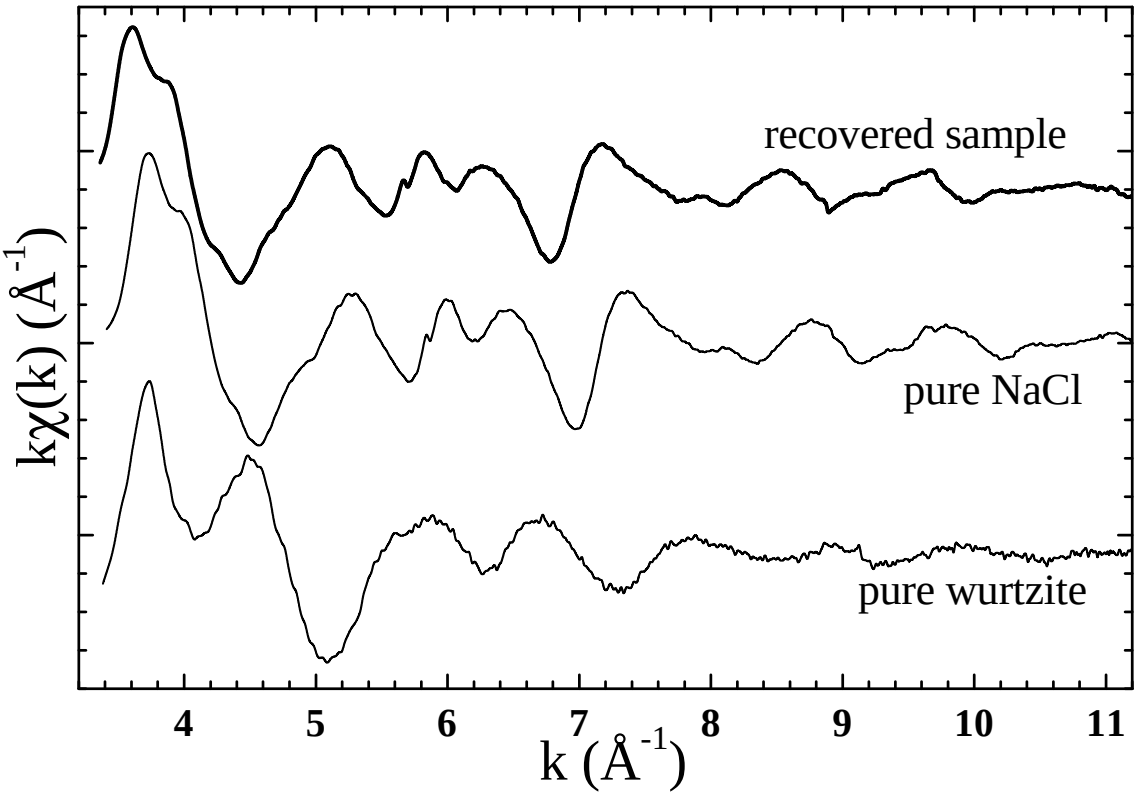

FIG. 2:

Figure 3

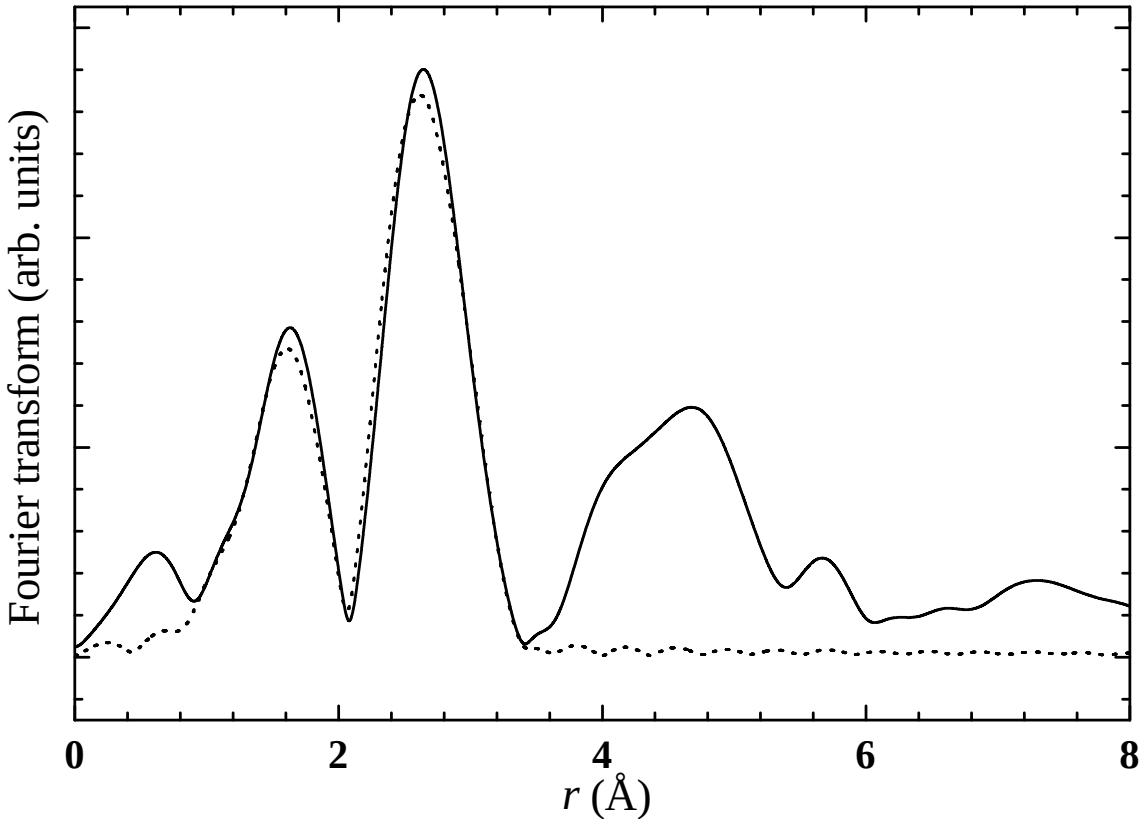

FIG. 3: