

A comprehensive study of structure and properties of nanocrystalline zinc peroxide

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Abstract

Nanocrystalline zinc peroxide (nano-ZnO₂) was synthesized through a hydrothermal process and comprehensively studied using several experimental techniques. Its crystal structure was characterized by X-ray diffraction, and the average crystallite size of 22 nm was estimated by Rietveld refinement. The temperature-dependent local environment around zinc atoms was reconstructed using reverse Monte Carlo (RMC) analysis from the Zn K-edge X-ray absorption spectra. The indirect band gap of about 4.6 eV was found using optical absorption spectroscopy. Lattice dynamics of nano-ZnO₂ was studied by infrared and Raman spectroscopy. *In situ* Raman measurements indicate the stability of nano-ZnO₂ up to 250 °C above which it decomposes into ZnO and O₂. The obtained experimental results were supported by first-principles density functional theory (DFT) calculations.

Keywords: ZnO₂, X-ray diffraction, X-ray absorption spectroscopy,

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1. Introduction

Zinc peroxide (ZnO_2) is a wide-band gap semiconductor that has been attracting the attention of scientists for several decades. It has many applications across a variety of industries: it is used by the rubber industry [1]; it is used in the production of plastics [2], in cosmetics and pharmacy [3]; it is an oxidant for explosives and pyrotechnic mixtures [4], and a precursor to ZnO [5, 6, 7, 8, 9, 10, 11, 12, 13, 14]; it is a photocatalyst [15, 16], a luminophore [17, 18]; it can be used to purify water [19] and as a detoxification agent against mustard gas [20]. Recently, antibacterial and antiviral properties of ZnO_2 nanoparticles were also reported [21, 22]. A progress report by Hu *et al.* published in 2021 summarizes and discusses the advances in the construction of versatile metal peroxide nanoparticles for disease-specific chemoreactive nanotherapeutics [23]. Finally, zinc peroxide was mentioned as a prospective material for rechargeable zinc-air batteries [24].

The phase transition of hexagonal ZnO into cubic ZnO_2 induced by hydrogen peroxide treatment on the surface of ZnO switching memory film is a prospective approach for making fully transparent analog memristor devices [25].

The reverse process of mechanochemical transformation of ZnO_2 into a highly defective ZnO was also discussed in the literature [26]. The production of a stable *p*-type ZnO phase remains a research goal in the development of ZnO -based optoelectronic devices, and ZnO_2 appears to be a suitable precursor to achieve a Zn-poor ZnO , which is a phase favorable towards *p*-type conductivity [9, 27].

To our knowledge, zinc peroxide has never been synthesized as a single-crystal and exists at ambient pressure in nanocrystalline (2-100 nm) form of cubic- ZnO_2 . A principal strategy for obtaining ZnO_2 nanoparticles is to oxidize reactive Zn species with hydrogen peroxide. However, the exact procedure (Zn-containing reactant, reaction temperature, stirring time, reaction medium, etc.) varies across sources and only in few cases pure nanocrystalline ZnO_2 was obtained, while in many cases the products are a mixture of zinc peroxide and zinc oxide in different forms. Reaction temperatures range from ambient [8, 28] to 100 °C and beyond [5, 17, 18]. Active Zn species are generated from either zinc oxide [17, 18, 28] or zinc acetate [5, 7, 29, 30, 31]. More exotic methods involve converting inorganic zinc salts into zinc-organic compounds [32, 33], or even laser ablation of metallic zinc [6].

In contrast to ZnO_2 nanoparticles, few studies are dedicated to ZnO_2 thin

films. Successive ionic layer adsorption and reaction (SILAR) techniques [10], electrochemical deposition [34], ZnO chemical conversion [35], as well as magnetron deposition at cryogenic temperature substrates [36] have been used to obtain ZnO₂ thin films.

The structural, optical, vibrational properties of ZnO₂ have been studied in the past by different experimental methods such as X-ray diffraction, X-ray absorption (XAFS), Scanning and Transmission electron microscopy (SEM, TEM), UV/VIS optical, Raman/IR and photoluminescence spectroscopies [7, 11, 29, 30, 31, 36, 37, 38, 39]. Cubic ZnO₂ has a pyrite structure (space group $Pa\bar{3}$ (No. 205), $a = 4.871$ Å [40]) with peroxide (O₂)²⁻ groups being shared between two neighbouring ZnO₆ octahedra (Fig. 1) [9, 32, 41, 42]. Peroxide bond length is 1.47 Å, being significantly shorter than the bond length between zinc and oxygen ions (2.11 Å). A large difference in electronegativity between zinc and oxygen atoms suggests a predominantly ionic bond character [11].

Upon heating at ambient pressure, ZnO₂ decomposes into hexagonal ZnO phase ($2\text{ZnO}_2(\text{s}) \rightarrow 2\text{ZnO}(\text{s}) + \text{O}_2(\text{g})$) with an exothermic peak around 200-230 °C [13, 43]. If the size of ZnO₂ nanocrystals decreases down to 2-3 nm, the transition occurs in a broader temperature range (180-250 °C) as demonstrated by in-situ XRD and EXAFS measurements [32, 39]. Moreover, a presence of an intermediate amorphous phase at the transition process [39] is suggested. The relatively low decomposition temperature is caused by unstable peroxide groups and local charge imbalance in the ZnO₂ structure [9, 11]. However, at room temperature, ZnO₂ is stable under a pressure up to 36 GPa [32].

The number of theoretical studies of ZnO₂ is still limited. Bulk modulus, band structure, and electronic density of states were calculated in [32] using the LDA approximation and plane-wave basis set. Magnetic, elastic, and optical properties of ZnO₂ were calculated using a plane-wave basis set with different functionals by Thapa et al. [44]. First-principles calculations predict the existence of dynamically and mechanically stable two-dimensional pentagonal ZnO₂ phase [45, 46, 47] as well as a ZnO₂ phase with $I4/mcm$ space group (No. 140) [48, 49], which becomes thermodynamically stable only above 120 GPa [50].

The experimentally reported band gap of ZnO₂ is in the range between 3.4 eV and 4.6 eV [30, 32, 41] and has indirect character with the valence band maximum located at Γ and with the conduction band minimum located between Γ and R points of the Brillouin zone [32]. First-principle calculations

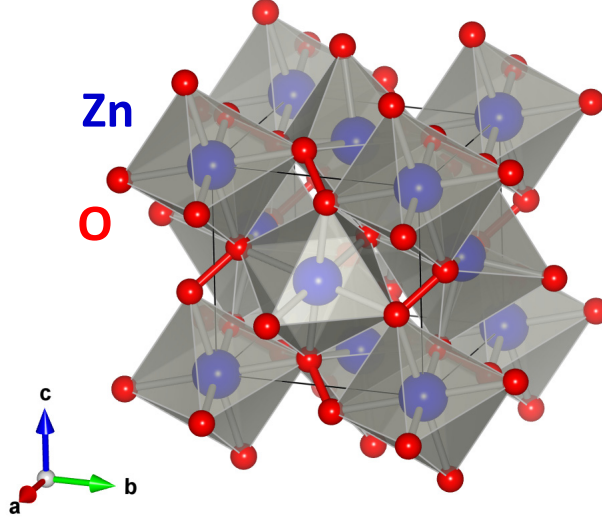


Figure 1: Crystallographic structure of ZnO_2 . The bonds between two oxygen ions forming O_2^{2-} anions are shown by red bars.

within the density functional theory (DFT) showed that there is a strong hybridization between Zn-d and O-p states in the valence band [32].

The dispersion in the structural, optical, and vibrational properties of nanocrystalline ZnO_2 comes from the nanocrystal sizes, morphology, and stoichiometry of zinc peroxide nanoparticles. Moreover, the mixed-phase compounds of ZnO_2 and ZnO or core-shell structure of ZnO_2/ZnO lead to a broader dispersion of the properties of studied samples. In contrast to ZnO , where point defects and defects induced by disordering are very well studied [51, 52], the role of disorder and defects in the structure of ZnO_2 is still largely unknown. Therefore, before ZnO_2 nanoparticles or thin films can be adopted for the next advanced applications, it is necessary to establish their exact local structure, as well as obtain a complete understanding of the contribution of disorder.

In the present work, we have carried out a systematic and comprehensive study of the properties of ZnO_2 nanoparticles by several experimental methods using the same sample. The local structure and lattice dynamics of ZnO_2 nanoparticles have been studied for the first time using synchrotron radiation X-ray absorption spectroscopy combined with advanced analysis based on reverse Monte-Carlo (RMC) simulations. The combination of ex-

perimental methods allowed us to carry out a multiscale study of ZnO₂: XAFS (short-range), Raman scattering (medium-range), and XRD concomitantly with SEM morphological imaging (long-range), similarly to a recent study [53].

2. Experimental

Nanocrystalline ZnO₂ (nano-ZnO₂) powders were produced by a hydrothermal process using zinc acetate as a precursor and hydrogen peroxide as an oxidizing agent. 11.4 g of zinc acetate dihydrate (Zn(CH₃COO)₂·2H₂O, Sigma-Aldrich, 99.999%) were dissolved in 750 ml of deionized water in a round-bottom flask with a dephlegmator and 70 ml of hydrogen peroxide (H₂O₂; mol.30%). The solution was heated up to 100 °C to conduct the hydrothermal reaction. Afterward, the solution was cooled down to room temperature, and ZnO₂ powder was extracted from the liquid and washed with deionized water. The material was finally dried in the air for 24 hours.

The crystallographic structure and crystallite size of nano-ZnO₂ were determined by the X-ray diffraction (XRD) technique. XRD measurements were performed using a PANalytical X’Pert PRO diffractometer equipped with the Cu (K α) anode X-ray tube and a multichannel solid-state detector. The X-ray tube operated at 45 kV and 40 mA. The diffraction pattern was recorded in the range of $2\theta = 10\text{--}140^\circ$ with a step size of $\Delta(2\theta) = 0.0263^\circ$.

The morphology and sizes of ZnO₂ nanoparticles were investigated by scanning electron microscope (SEM) Tescan Lyra3, equipped with a high brightness Schottky emitter. SEM images were taken using beam accelerating voltage 15 kV and beam current 100 pA.

The local atomic structure of nano-ZnO₂ powder was studied using the X-ray absorption spectroscopy at the HASYLAB/DESY PETRA-III P65 Applied XAFS beamline [54]. The PETRA-III storage ring operated at $E=6.08$ GeV and current $I=95$ mA in top-up 40 bunch mode. Temperature-dependent X-ray absorption spectra were recorded at the Zn K-edge in transmission mode using two ionization chambers located before and after the sample. The X-ray beam from an undulator was monochromatized using a fixed-exit Si(111) double-crystal monochromator. The harmonic rejection was achieved by an uncoated silicon plane mirror. An Oxford Instruments liquid helium flow cryostat was used to maintain the sample temperature in the range of 10–300 K. The sample was prepared from ZnO₂ powder, which was gently milled in an agate mortar and deposited on a Millipore membrane.

The sample thickness was adjusted to give the value of the absorption edge jump $\Delta\mu=1$.

Optical properties of nano-ZnO₂ powder were studied by a JASCO V-660 UV/VIS double-beam spectrophotometer equipped with deuterium and tungsten iodine lamps in the range of 200–800 nm at room temperature with an optical resolution of 1.0 nm.

Optical absorption spectra were measured on UV-Vis spectrometer Jasco V-660. The V-660 is a double-beam spectrophotometer utilizing a double monochromator and a photomultiplier tube detector. Spectra of the ZnO₂ nanopowders were recorded at room temperature in the wavelength range of 200–800 nm with a scan rate of 5 nm/s and resolution of 1.0 nm at room temperature. CaF₂ was used in the measurements as a substrate and reference.

Vibrational properties were characterized using FTIR and Raman spectroscopies. A vacuum Fourier transform infrared spectrometer Bruker VERTEX 80v was used to measure the infrared spectrum of a pellet in the energy range 50–600 cm⁻¹ where theoretically predicted IR peaks lie. The pellet was prepared from mechanically mixed nano-ZnO₂ and KBr powders, and then the mixture was compressed using a standard KBr pellet method. Note that the long-wavelength border of the spectrum is limited to 200 cm⁻¹ due to the border of the transparency of the pellet. Temperature-dependent Raman scattering spectra were collected by a Renishaw micro-Raman spectrometer under the excitation at 514.5 nm. The sample temperature was controlled by the Linkam THMS350V stage. The optical chamber was weakly blown through with 99.999% purity nitrogen during the measurements.

3. Results

3.1. X-ray Diffraction and SEM

X-ray diffraction pattern of nano-ZnO₂ (Fig. 2) does not contain any impurity phases. All peaks can be assigned to the ZnO₂ phase with a $Pa\bar{3}$ (No. 205) space group. Initial lattice parameters and atomic coordinates for the Rietveld refinement were taken from [32]. Rietveld refinement was performed with the BGMN [55] software using the Profex code [56] and resulted in a very good fit. Some discrepancies between the calculated and experimental diffraction patterns can only be seen for the most intense peaks of the diffraction pattern, but the peaks at higher scattering angles show excellent agreement with the experiment (see the inset in Fig. 2).

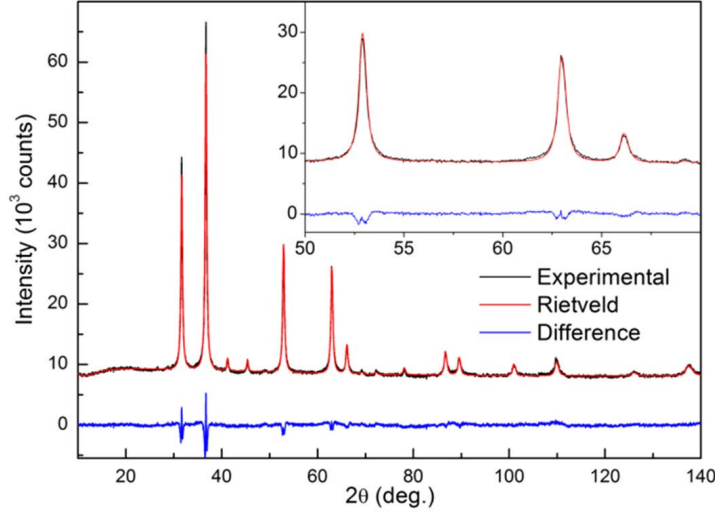


Figure 2: Experimental and calculated diffraction patterns of nano-ZnO₂; inset shows the enlarged part of the diffraction pattern between 50° and 70°.

Crystallite size obtained from Rietveld refinement is $d=22$ nm. Although the parameter responsible for the microstrain modeling was set to be refined, it converged to zero indicating that no microstrain is present in the sample. The crystallographic parameters obtained by refinement are reported in Table 1. Our experimental XRD pattern of ZnO₂ sample and crystallographic parameters agree well with the experimental data obtained for ZnO₂ nanopowder in the previous studies [11, 30, 31, 57].

The insight into the morphology of the prepared ZnO₂ nanopowder was obtained by using SEM measurements. Fig. 3 shows hollow sphere or rounded-

Table 1: Crystallographic parameters of nano-ZnO₂ obtained by Rietveld refinement. Space group $Pa\bar{3}$ (No. 205), the lattice parameter $a_0=4.89314(14)$ Å, the atomic displacement parameter B_{iso} , the weighted profile R-factor $R_{\text{wp}}=2.35\%$, the expected R-factor $R_{\text{exp}}=1.07\%$ and the goodness-of-fit $\chi^2=4.82$ [58].

Atom	Wyckoff position	Fractional coordinates			B_{iso} (Å ²)
		x	y	z	
Zn	4a	0	0	0	1.679(20)
O	8c	0.41309(27)	0.41309(27)	0.41309(27)	4.35(11)

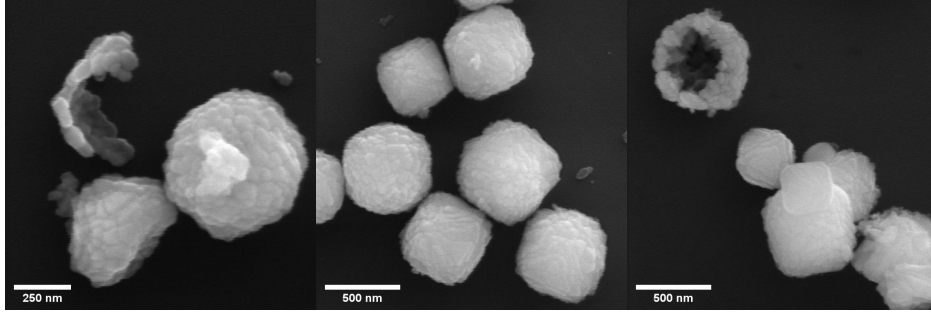


Figure 3: SEM images of the as-prepared nanopowder ZnO_2 : nanocrystals of 20–40 nm in diameter agglomerate in hollow microspheres or rounded cubes with diameters around 500 nm.

cube structures whose shells are composed of uniform ZnO_2 layered nanocrystals with a thickness of several tenths nanometers, the size of the structures is around 200–500 nm.

3.2. Optical Absorption Spectroscopy

The absorption spectrum of nano- ZnO_2 is shown in Fig. 4. The optical band gap was determined using absorbance (A) as a function of photon energy. The intersection between the extrapolation of the linear part of the curve and the axis $A=0$ gives the optical band gap value of 4.6 eV. This value is in good agreement with the 4.5 eV value obtained using the same method by J.E. Morales-Mendoza *et al.* in [30]. The discrepancy is seen with the values (3.13–3.25 eV) reported in [20], however, this could be associated with the large porosity of the sample used in their research.

3.3. Infrared and Raman Spectroscopy

The infrared spectrum (Fig. 5) of nano- ZnO_2 has four absorption bands in the far-infrared range at about 210, 274, 349 and 434 cm^{-1} (Table 2).

In-situ temperature-dependent Raman scattering spectra of nano- ZnO_2 (Fig. 6) were recorded on an as-prepared sample upon heating in air at the temperatures 120, 250 and 270 $^{\circ}\text{C}$. Three bands due to the ZnO_2 phase were identified at 410, 471 and 838 cm^{-1} in the Raman scattering spectrum up to 250 $^{\circ}\text{C}$. Thermal decomposition of ZnO_2 to ZnO was observed at around ≈ 250 $^{\circ}\text{C}$. At higher temperatures, three new bands of nanocrystalline ZnO were identified at 330, 436, 582 cm^{-1} in agreement with the frequency values from [59].

Table 2: Comparison of the calculated and experimental frequencies of the phonon modes in ZnO₂.

Calculated				Frequency (cm ⁻¹)		Symmetry	Activity	Types
CRYSTAL		VASP	this study	Experimental				
WC1LYP	PBE0	PBE0		other studies				
143.2	142.5	135.1				F _u	IR	Lattice
143.5	143.3	136.0				E _u		Lattice
151.9	153.2	147.3				A _u		Lattice
208.1	208.9	199.3	210			F _u	IR	Lattice
271.3	274.3	266.1	274			F _u	IR	Lattice
306.2	307.9	304.0				A _u		Lattice
342.5	347.1	338.7	349			F _u	IR	Lattice
369.6	374.7	364.8				E _u		Lattice
408.7	416.2	408.9	410	407 [11], 410 [30], 414.2 [20], 411 [37], 410 [38], 410 [60]		F _g	Raman	O ₂ ²⁻ libration
419.5	425.5	421.0				E _g	Raman	O ₂ ²⁻ libration
428.2	431.8	423.1	434	429 [18], 436.5 [29]		F _u	IR	Lattice
477.1	485.6	482.6	471	483 [11], 476.3 [20], 473 [30], 472 [37], 478 [38], 475 [60]		F _g	Raman	O ₂ ²⁻ libration
916.8	977.9	975.2	838	835 [11], 840.7 [20], 838 [30], 838 [37], 842 [38], 840 [60]		A _g	Raman	O ₂ ²⁻ stretching
918.6	978.7	974.9		1080.8 [20], 871 [30], 936 [37], 960 [38], 937 [60]		F _g	Raman	O ₂ ²⁻ stretching

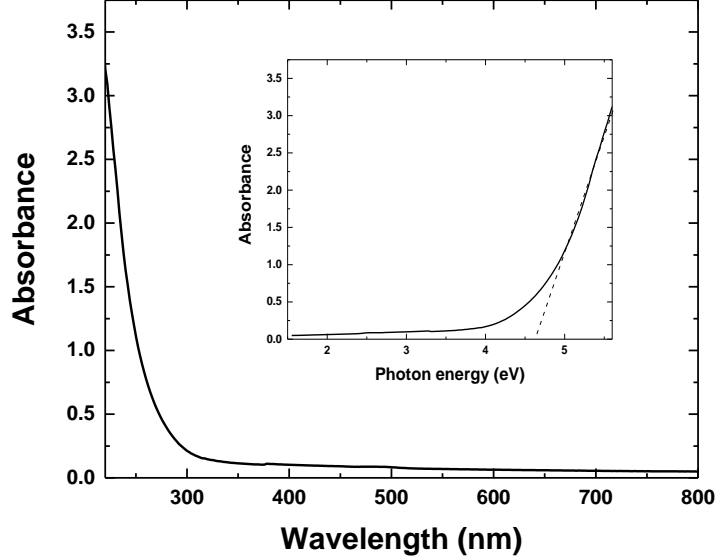


Figure 4: Optical absorption of nano-ZnO₂. $(Ah\nu)^{1/2}$ as a function of $h\nu$ for the nanocrystalline ZnO₂.

3.4. X-ray Absorption Spectroscopy

X-ray absorption spectra of nano-ZnO₂ powder, measured at 10, 150, and 300 K, were analyzed using the reverse Monte Carlo (RMC) method based on the evolutionary algorithm (EA), implemented in the EvAX code [61]. The review of the method can be found in [62], and its recent application in the analysis of complex material CuMo_{1-x}W_xO₄ in [63, 64]. The use of the RMC method in the analysis of ZnO₂ EXAFS allowed us to extract reliable structural information for coordination shells up to 8 Å.

First, the extended X-ray absorption fine structures (EXAFS) $\chi(k)k^2$ (Fig. 7) were extracted using a conventional procedure [65]. Note the high quality of the obtained EXAFS with a large signal/noise ratio. Upon increasing temperature from 10 to 300 K, the EXAFS oscillations become damped at the high- k values due to thermal disorder. The structural contributions from coordination shells up to 8 Å are well visible in the Fourier transforms of EXAFS. The first two dominating peaks at 1.5 Å and 3.0 Å are mainly due to 6 oxygen atoms of the first coordination shell ($r(\text{Zn-O}_1) = 2.11$ Å) and 12 zinc atoms of the third coordination shell ($r(\text{Zn-Zn}_3) = 3.46$ Å), respectively. A more detailed interpretation of the EXAFS signals will be given below.

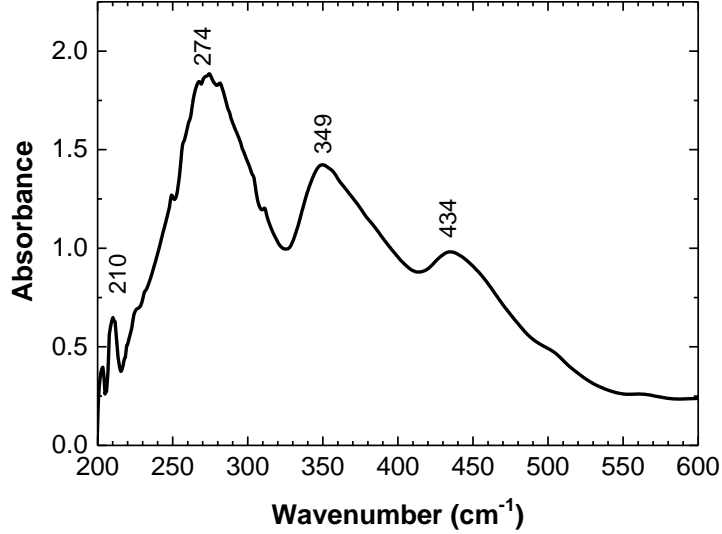


Figure 5: The infrared spectrum of nano-ZnO₂ in the range of 200–600 cm⁻¹.

To perform RMC analysis of EXAFS, $4a_0 \times 4a_0 \times 4a_0$ simulation boxes (supercells) with periodic boundary conditions (PBC) were constructed, referencing the ZnO₂ ($Pa\bar{3}$) crystallographic structure [11]. RMC/EA calculations were performed for 32 atomic configurations. At each iteration, the new atomic configuration was generated by randomly displacing all atoms in the simulation box with the maximally allowed shift of 0.4 Å to get the best possible agreement between the Morlet wavelet transforms (WTs) [66] of the experimental and calculated EXAFS spectra. The calculations were performed in the k -space range from 2.5 to 13 Å⁻¹ and in the R -space range from 0.8 to 7.5 Å. No significant improvement in the residual was observed after 5000 iterations. Note that there is a small difference between the positions R of the peaks in FTs and the crystallographic values r due to the phase shifts present in EXAFS.

The configuration-averaged EXAFS spectra were calculated by ab initio real-space multiple-scattering (MS) FEFF8.50L code [67], including the MS effects up to 8th order. The scattering potential and partial phase shifts were calculated only once within the muffin-tin (MT) approximation [68] for the cluster with a radius of 4.0 Å, centered at the absorbing Zn atom and constructed based on crystallographic ZnO₂ structure [11]. Small variations of the cluster potential due to atom displacements during the

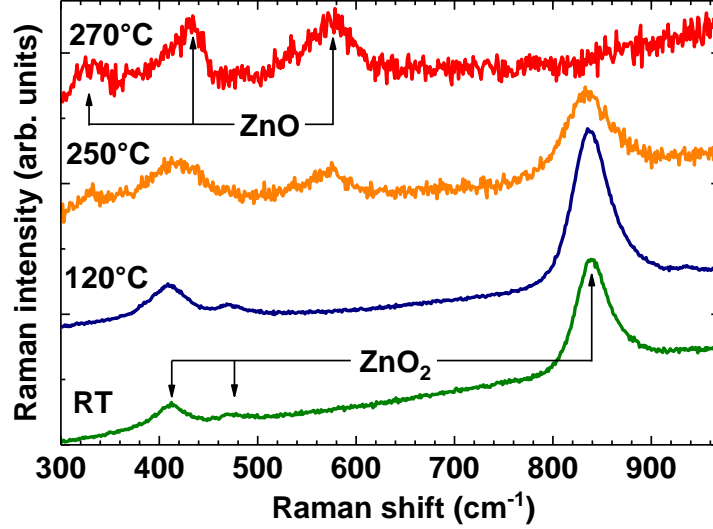


Figure 6: Evolution of the Raman scattering spectrum of nano-ZnO₂ upon heating from room temperature to 270 °C.

RMC/EA simulations were neglected. The photoelectron inelastic losses were accounted for within the one-plasmon approximation using the complex exchange-correlation Hedin-Lundqvist potential [69]. The amplitude reduction factor S_0^2 is included in the scattering amplitude [68], calculated by the FEFF code, and no additional correction of the EXAFS amplitude was performed.

The result of the RMC/EA analysis is shown in Fig. 8. The model reproduces well the experimental data in both k and R space at all temperatures, suggesting that the average structure determined by XRD gives a good starting model to fit the EXAFS data. An increase in temperature from 10 to 300 K leads to an increase in thermal disorder, which more strongly affects peaks beyond the first coordination shell ($r > 2$ Å). Partial radial distribution functions (RDFs) $g_{\text{Zn-O}}(r)$ and $g_{\text{Zn-Zn}}(r)$ were calculated from the coordinates of atoms in the supercell and are shown in Fig. 9.

The atomic coordinates in the RMC simulation boxes were used to extract information on the mean-square displacements (MSDs) of atoms and the mean-square relative displacements (MSRDs) for atom pairs [61]. The MSRDs for Zn-O and Zn-Zn atom pairs were evaluated for the first three peaks, corresponding to the O₁, O₂, and Zn₃ coordination shells. The MSDs for oxygen and zinc atoms were also determined, taking into account the

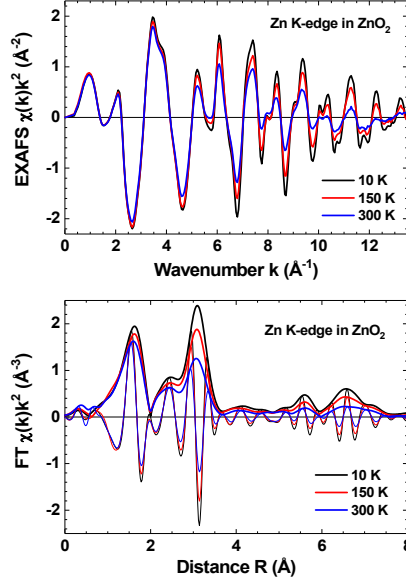


Figure 7: Experimental Zn K-edge EXAFS $\chi(k)k^2$ spectra and their Fourier transforms (FTs) of nano-ZnO₂ at 10, 150 and 300 K. Note that the positions of peaks in the FTs were not corrected for the phase shift, therefore, they are located at slightly shorter than crystallographic distances.

displacement of O and Zn atoms from their equilibrium positions.

The difference between MSRD_{AB} for the atom pair A–B and a sum of MSD_A and MSD_B gives the displacement correlation function (DCF) [70]

$$2\text{DCF}_{\text{AB}} = \text{MSRD}_{\text{AB}} - (\text{MSD}_\text{A} + \text{MSD}_\text{B}). \quad (1)$$

Note that at long distances the correlation of atomic motion vanishes and $\text{DCF}=0$. This fact allows determining both MSRD and MSD factors from a single EXAFS spectrum when reliable analysis of distant coordination shells is possible [71]. The temperature dependence of the MSRD and MSD factors in ZnO₂ for the first three coordination shells is shown in Fig. 10. Weak variation of the MSRD s with increasing temperature indicates a rather strong bonding between Zn and nearest O and Zn atoms. Moreover, the near-neighbor atomic motions are strongly correlated, as evidenced by a large difference between MSRD factors and a sum of respective MSD s.

The thermal dependence of the MSRD factors was described by a sum of static and vibrational disorder contributions using the correlated Einstein

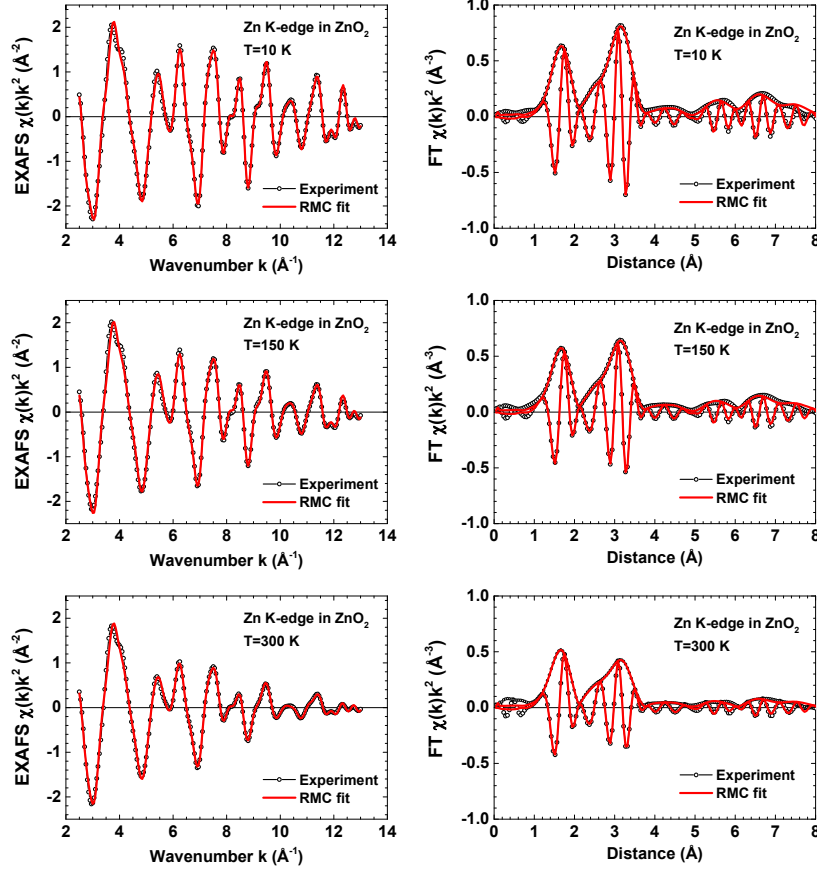


Figure 8: Results of RMC/EA-EXAFS calculations for nano-ZnO₂ at 10 and 300 K: comparison of the experimental and calculated (RMC/EA) Zn K-edge EXAFS spectra $\chi(k)k^2$ (left panels) and their Fourier transforms (FTs) (right panels).

model [72] (see dashed lines in Fig. 10). The characteristic Einstein temperatures θ_E were determined to be 400 K for Zn–O₁, 320 K for Zn–O₂, and 220 K for Zn–Zn₃ atom pairs. The static contribution to MSDs was estimated to be about 0.005–0.006 Å².

3.5. First-Principles Calculations

Experimental studies are accompanied by ab initio quantum chemistry calculations which were performed using the method of a linear combination of atomic orbitals (LCAO) as realized in the CRYSTAL17 code [73]. For a complete representation, the calculations were also done using a plane wave

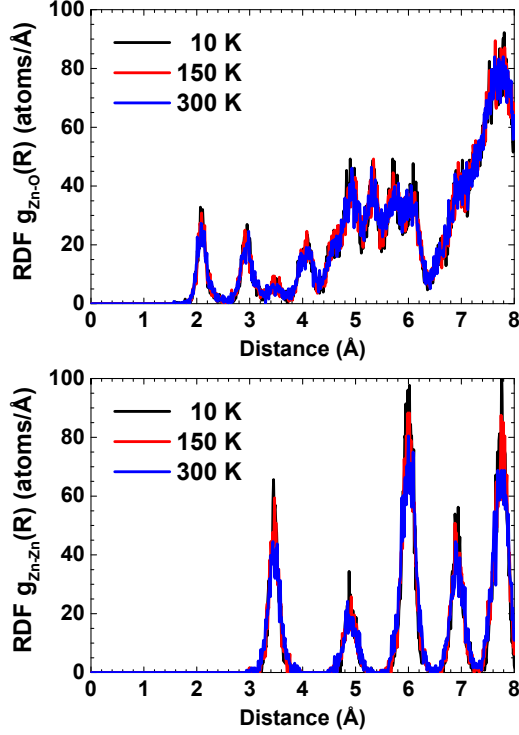


Figure 9: Temperature dependence of the partial radial distribution functions (RDFs) $g(\text{Zn-O})$ and $g(\text{Zn-Zn})$ calculated from the results of RMC/EA simulations.

(PW) approach as implemented in the VASP code [74, 75].

Based on XRD data (Table 1), ZnO_2 was modelled using the crystallographic structure belonging to a space group No. 205 ($Z=4$, $Pa\bar{3}$), with Zn atoms occupying Wyckoff position $4a$, and O atoms located at position $8c$, with a total of 12 atoms (4 Zn and 8 O) in the unit cell.

LCAO calculations, including analyses of phonon frequencies and vibration intensities, were performed using algorithms as implemented in CRYSTAL17 code [73, 76, 77, 78, 79]. All-electron atom-centered sets of Gaussian-type functions were used to describe atoms. For Zn, the $(86s)$ $(4111sp)$ $(41d)$ basis set was adopted from Gryaznov *et al.* [80, 81], while for O the $(8s)$ $(411sp)$ $(1d)$ basis set was taken from Bredow *et al.* [82]. Having considered multiple formulations of the exchange-correlation functional of the DFT, we settled for WC1LYP, a 1-parameter functional that combines the WC exchange functional with 16% of Hartree-Fock exchange and the LYP correlation functional

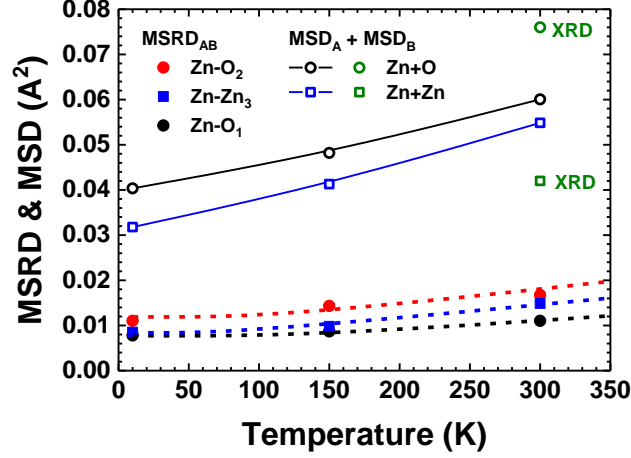


Figure 10: Temperature dependence of the MSD (open symbols) and MSRD (solid symbols) factors in nano-ZnO₂ calculated from the results of RMC/EA simulations. The MSRD factors are given for the first three coordination shells of zinc (O₁, O₂ and Zn₃). Dashed lines correspond to the correlated Einstein models (see text for details). The MSD factors obtained by XRD at 300 K are also shown for comparison. The values of the MSD factors are given for a pair of atoms, i.e they are equal to the sum of MSD for Zn and O/Zn atoms.

[83]. For the sake of comparing Gaussian basis set to a plane-wave basis set, we also include results obtained with the PBE0, a hybrid version of the PBE exchange-correlation functional with 25% of HF exchange [84]. Reciprocal space was sampled using a Monkhorst-Pack mesh [85] with a shrinking factor of 16, which yielded 249 points in the irreducible part of the Brillouin zone. The self-consistent field (SCF) convergence on the difference in total electronic energy was set to 10^{-10} hartree for geometry optimization and phonon frequency calculations. Additionally, we evaluated the values of the MSD parameters at different temperatures using tensors of anisotropic displacement parameters (ADP) obtained with a scheme described in [86] and implemented in the CRYSTAL17 code [73].

The PW calculations using the Vienna *ab initio* simulation program VASP version 5.4.4 [74, 75] were performed for a 12-atom ($1 \times 1 \times 1$) unit cell using a $4 \times 4 \times 4$ Γ -centered Monkhorst-Pack \mathbf{k} -point mesh using the projector augmented wave (PAW) method. The valence electron configurations of the PAW pseudopotentials for Zn and O were ($3d^{10}, 4s^2$) and ($2s^2, 2p^4$), respectively. Cut-off energy of 600 eV for the expansion of the plane wave

Table 3: The band gap E^{gap} (in eV) and the lattice parameter a_0 as well as the Zn–O and O–O bond distances d^{ZnO} and d^{OO} (all in Å) obtained with the hybrid functionals PBE0 [84] and WC1LYP [83] for the fully relaxed ZnO_2 structure are listed. α^{HF} specifies the portion of exact exchange employed with actual hybrid functional compared with published experimental data for structure [11] and band gap [32, 41, 30].

Code	Functional	α^{HF}	a_0	d^{ZnO}	d^{OO}	E^{gap}
CRYSTAL	PBE0	0.25	4.889	2.106	1.479	5.39
	WC1LYP	0.16	4.902	2.109	1.502	4.23
VASP	PBE0	0.25	4.890	2.110	1.458	5.25
	PBE0	0.20	4.902	2.114	1.465	4.63
Experiment			4.893	2.109	1.473	3.8-4.6

Table 4: The sums of the MSD factors at different temperatures for the Zn+Zn and Zn+O atom pairs (in Å²) obtained from calculations using anisotropic displacement parameter tensor as implemented in CRYSTAL code.

Temperature	Zn+Zn	Zn+O
0 K	0.0024	0.0037
150 K	0.0038	0.0047
300 K	0.0066	0.0072

basis set was employed to ensure well-converged energies ($<10^{-8}$ eV) and atomic forces ($<10^{-3}$ eV/Å) for the structural relaxations and the phonon calculations. For a better comparison of the PW and LCAO approaches, hybrid functionals were used also in the calculations by VASP. An admixture of 25% (the default value for PBE0) and 20% of Hartree-Fock (HF) exact exchange α^{HF} were employed. The value of 20% shows the effect of an exact exchange reduction in comparison to the hybrid functional WC1LYP, which includes only 16% of HF exact exchange.

The calculated values of the band gap E^{gap} , the lattice parameter a_0 as well as the Zn–O and O–O bond distances for the fully relaxed ZnO_2 structure using both series of calculations (CRYSTAL17 and VASP) are reported in Table 3. Frequencies of the phonon modes are compared with the experimental data in Table 2. The MSD parameters calculated for three selected temperatures (0 K, 150 K, and 300 K) using the CRYSTAL17 code are given in Table 4.

3.6. Discussion

Nanocrystalline ZnO_2 synthesized in the present work is a wide-band gap (4.6 eV) insulator, and its crystallographic structure is influenced by the size effect. The structure was studied by two complementary techniques, XRD and EXAFS, which probe long-range and short-range orders, respectively. The lattice parameter a_0 of our sample (Table 1) corresponds well to that reported previously in the literature [11, 30, 31, 32, 57]. Its nanocrystalline nature (crystallite size $d = 22$ nm) appears as a broadening of Bragg peaks in the XRD pattern in Fig. 2 and leads to some crystal structure relaxation, which can be expected to be larger near the crystallite surface or around defects (for example, oxygen vacancies [17]) located within the crystallites. Such relaxation introduces static disorder into the regular crystal lattice and promotes a variation of interatomic distances leading to the broadening of peaks in the partial RDFs $g_{\text{Zn-O}}(r)$ and $g_{\text{Zn-Zn}}(r)$ in Fig. 9. The MSD factors can be evaluated from the atomic displacement parameters B_{iso} (Table 1) and are equal to $\text{MSD}_{\text{XRD}}(\text{Zn})=0.021 \text{ \AA}^2$ and $\text{MSD}_{\text{XRD}}(\text{O})=0.055 \text{ \AA}^2$. Note that they include contributions from a reduced crystallite size and thermal disorder.

SEM measurements show the complex structure of powder, visualizing the hollow spherical or rounded-cube shape of agglomerated particles with dimensions of about 200–500 nm. The surface of particles is formed by the mosaic structure of spliced nanoparticles with 20–40 nm diameter that is clearly seen from the layered particle in the upper left corner (left panel) in Fig. 3.

To distinguish thermal and static disorder, the temperature dependence of the obtained MSRD factors for Zn–O and Zn–Zn atom pairs was described by the correlated Einstein model (dashed lines in Fig. 10), and the contribution of the static disorder was estimated to be about 50–60%. At the same time, the large difference between the sum of two MSD factors and the MSRD factors indicates a significant amount of correlation in the vibrational motion of the nearest atoms.

Properties of calculated and experimentally observed ZnO_2 fundamental vibrations are listed in Table 2. Group theory predicts five IR-active and five Raman-active modes. Three distinct bands due to vibrations of O_2^{2-} anion are observed in the calculated Raman spectrum: a band consisting of two peaks around $\sim 410\text{--}420 \text{ cm}^{-1}$ (O–O libration, a rotation along an axis perpendicular to the bond), a band at $\sim 470\text{--}480 \text{ cm}^{-1}$ (libration), and the major band consisting of two peaks above 900 cm^{-1} (O–O bond stretching).

Calculated vibrational modes of O_2^{2-} anion show localized nature and the anion behaves like a single particle, rather than allowing independence to its constituent atoms. All the molecular stretching and libration vibrations of O_2^{2-} anion are Raman-active. In all Raman-inactive vibrational modes, the O–O fragment moves as a rigid body (both atoms have identical translation vectors). In contrast, all Raman-active modes are comprised exclusively of translations that bend, stretch and rotate O–O bond relative to stationary Zn atoms. Conversely, the lattice vibrations are Raman-inactive and only a part of those are IR-active (Table 2).

Calculated vibration frequencies are in good agreement with the experimentally observed Raman and IR frequencies [11, 20, 30, 37, 38, 60]. These results are in good relation to the performed measurements (410, 471 and 838 cm^{-1}). The experimental Raman spectra showed only one stretching band at 838 cm^{-1} and two libration bands at 410 and 471 cm^{-1} due to the overlap of broad Raman bands. They also agree with previously reported results: 840 cm^{-1} attributed to O–O bond stretching [87]. Peaks at 835, 483, and 407 cm^{-1} are reported by Escobedo-Morales *et al.* [11], with the first, most intense signal being attributed to the stretching of the O–O bond, while two other signals are left uninterpreted. Experimentally measured IR peaks at 210, 274, 349, and 434 cm^{-1} are in good agreement with the calculated ones. The peak located at 434 cm^{-1} was also previously reported in the literature [18, 29]. The theoretically predicted IR band at 143 cm^{-1} was not observed in our experiments due to the KBr pellet not being transparent in this region.

The experimental MSD parameters (Fig. 10) obtained by the RMC simulations from the Zn K-edge EXAFS can be compared with those calculated (Table 4) and estimated by XRD. The two sets of the calculated MSD parameters for Zn–O and Zn–Zn atom pairs differ significantly for each temperature with the experimental values being larger. The calculated MSD values include only vibrational contributions, whereas the static disorder present in the ZnO_2 nanoparticles dominates the experimental MSD values obtained from the EXAFS and XRD data. As a result, the calculated MSDs are an order of magnitude lower than the experimental ones. The MSD values obtained by RMC and XRD are in reasonable agreement taking into account the weak sensitivity of powder XRD data to the atomic displacement parameters B_{iso} (Table 1) [88].

4. Conclusions

A comprehensive study of nanocrystalline ZnO_2 has been performed using several experimental methods and first-principles calculations.

The sample was produced by a hydrothermal process using zinc acetate as a precursor and hydrogen peroxide as an oxidizing agent. Rietveld refinement of the X-ray diffraction pattern confirmed cubic- ZnO_2 structure belonging to the space group $Pa\bar{3}$ (205) with a short peroxide O–O bond distance (1.47 Å). The crystallite size was estimated to be about 22 nm. The indirect band gap of about 4.6 eV was found using optical absorption spectroscopy. High-resolution SEM images were taken to study ZnO_2 morphology.

The local atomic structure around zinc atoms was probed for the first time by the Zn K-edge EXAFS spectroscopy in combination with the reverse Monte Carlo simulations, which made it possible to determine the partial Zn–O and Zn–Zn RDFs. The analysis of partial RDFs $g_{\text{Zn–O}}(r)$ and $g_{\text{Zn–Zn}}(r)$ allowed us to estimate MSD factors for the Zn–O and Zn–Zn atom pairs and MSD factors of O and Zn atoms. Both MSD and MSDR factors have unusually large values, which were explained by the local structure relaxation due to the size effect. The large values of the MSD factors obtained by RMC are in reasonable agreement with those calculated from the atomic displacement parameters B_{iso} , obtained by the XRD method. The static and vibrational contributions to the MSDs were separated using the correlated Einstein model, and the Einstein temperatures θ_E were determined for the three nearest coordination shells.

Thermal decomposition of ZnO_2 to wurtzite ZnO around 250 °C was observed by temperature-dependent Raman spectroscopy. Below 250 °C, the Raman spectrum of ZnO_2 is dominated by the libration and stretching vibrational modes of O_2^{2-} anion, whereas its far-infrared spectrum contains only lattice modes. The detailed analysis of the fundamental vibrations of the ideal ZnO_2 crystal was performed using the hybrid exchange density functional theory within the LCAO and plane wave approaches. Both theoretical models predicted the equilibrium geometries, wide-band gap, and phonon frequencies in good agreement with the experimental results. The temperature dependence and smallness of the calculated MSD factors compared to those obtained from the analysis of XRD and EXAFS confirmed the significant contribution of the static disorder to their experimental values.

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