

An Electron Density Residual Study of Zinc Oxide

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The electron density distribution in zinc oxide [ZnO, hexagonal, $P6_3mc$, $a = 3.2489(1)$, $c = 5.2053(4)$, $Z = 2$], has been studied with X-ray single-crystal diffraction methods. Difference Fourier analysis did not reveal any strong interstitial residual electron density accumulation, suggesting strong ionicity of this compound. Similarly, in contrast to previous studies, no significant residuals at interstices could be detected from comparison of the observed structure factors of the red sample, annealed in zinc vapor, against the untreated white. [White sample: 278 equivalent-averaged reflections, $R = 0.016$; Red sample: 262 equivalent-averaged reflections, $R = 0.014$]. © 1996

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INTRODUCTION

Partly due to its various applications for electronic devices, ZnO has been a subject of study in many previous works. Physical properties such as coloration or electric conductivity varies with addition of dopants and heat treatment. Substitution of the Zn site or occupation of interstitial positions have been proposed as causes of this variation (1–4). However, chemical analyses (3–7) or Hall data (2) on red-colored varieties have always indicated excess of Zn of only less than 0.1%.

A single-crystal X-ray diffraction study comparing the electron density of a white crystal of ZnO with a heat-treated red one (4) showed a significant increase of $>2e/\text{Å}^{-3}$ in the interstitial position of the red crystal, suggesting excess Zn of up to 1.5%. This work, however, is based on a projected difference Fourier section synthesized from structure factors derived from measured diffraction intensities of an unmentioned number of only the $hk0$ reflections of the red vs the white crystal with no positional information along the z direction. It has thus been decided to reexamine this structure with our present-day methods.

EXPERIMENTAL

Single crystals of ZnO, one colored white with no thermal treatment and the other a red sample which was converted from white by holding at 1000°C for 10 h under Zn vapor in equilibrium with liquid Zn, were broken into several pieces for experiment. Cell constants were obtained from the setting angles of three crystals of each color (24 reflections; $108^\circ < 2\theta < 117^\circ$; graphite-monochromated $\text{MoK}\alpha_1$ radiation, 0.70926 Å). The average for white crystals was $a = 3.2488(1)$ and $c = 5.2054(1)$ Å and for red crystals, $a = 3.2490(1)$ and $c = 5.2052(6)$ Å; the scatter of averaging is in parentheses. Though the cell parameters presented here have larger e.s.d.'s than those listed in (4), the significant expansion which was seen in the c axis (5.2055(1) Å to 5.2069(1) Å) cannot be seen in the present results. The overall average ($a = 3.2489(1)$, $c = 5.2053(4)$ Å) has been adopted as the cell constant of ZnO determined in this study.

For intensity data collection, crystals were broken into equidimensional polyhedra (not grounded into spheres since this seemed to broaden the already broad diffraction profiles considerably) of approximate diameters 0.33 mm (white) and 0.28 mm (red). Intensity data were collected with a Rigaku automated four-circle diffractometer AFC-5 ($\text{MoK}\alpha$, 0.7107 Å; 40 kV, 30 mA). The 2θ - ω scan mode was used with scan widths $3.0 + 0.35 \tan \theta^\circ$ (white)/ $2.5 + 0.35 \tan \theta^\circ$ (red) in ω , speed $16^\circ/\text{min}$, maximum of 3 repeated measurements until $100\sigma(I) < I$. Reflections were measured in full reciprocal space ($|h| \leq 6$, $|k| \leq 6$, $|l| \leq 12$, $2\theta \leq 120^\circ$, $\sin \theta/\lambda \leq 1.215$).

[Hexagonal $P6_3mc$; $Z = 2$; $D_x = 5.680$; $F000 = 76$; $\mu = 254/\text{cm}$; $T = 296$ K; Lp corrections applied; empirical absorption corrections with DIFABS (8) run after isotropic refinement of z of oxygen and the scale parameter with fixed temperature factors (0.64 Å^2 for both Zn and O of

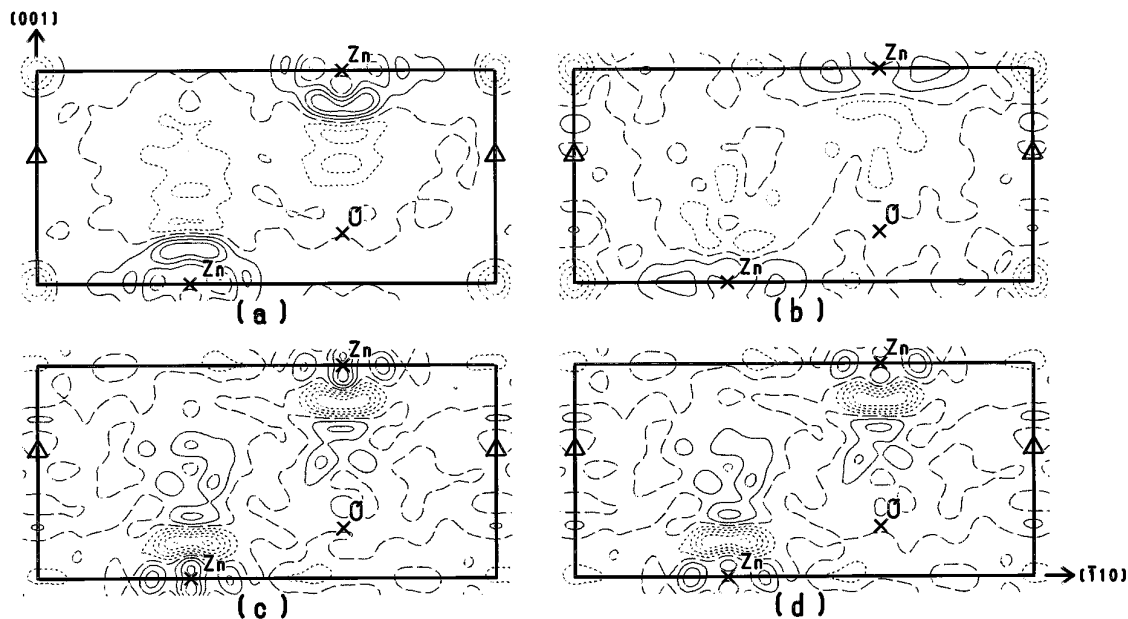


FIG. 1. Difference Fourier sections ($F_o - F_c$ for (a) white and (b) red samples; (c) $F' - F$; (d) $D' - D$) of a plane cut along the c axis and the diagonal connecting the acute edges of the rhombic face of the unit cell, which passes through the atomic positions (indicated by crosses) and the center of the interstitial position (triangles). The area of rectangular cell is $\sqrt{3}a \times c/2$. The increment of contours is $0.5e/\text{\AA}^3$; zero contours in broken lines and negative contours in dotted lines. Maximum and minimum heights in $e/\text{\AA}^3$: (a) $-1.47, +1.98$; (b) $-1.81, +1.30$; (c) $-2.58, +1.75$; (d) $-2.56, +1.40$.

the two samples) derived from preliminary refinement with spherical absorption correction tentatively applied using the approximate diameters; transmission factors 0.46–1.66 (white), 0.55–1.35 (red); 2370 nonabsent reflection intensities averaged into 278 independent data; all equivalents were observed with $|F_o| \geq 6\sigma(F_o)$, thus, used for refinement for the white crystal, 262 for the red; internal agreement among equivalents $R_{\text{int}} = 0.009$ (white), $R_{\text{int}} = 0.012$ (red); Final $R = 0.016$, $R_w = 0.015$ (white); $R = 0.014$, $R_w = 0.013$ (red).]

DISCUSSION

The structures of the two crystals were refined with RADY (9) using fully ionized scattering factors (10, 11), dispersion correction values (12), and correcting for extinction (type II isotropic). The number of equivalents were allotted as the weight. The enantiomorph for the red crystal was found to be opposite of the white; the reflection data used were reset to the same enantiomorph in order to facilitate comparison. The final R values for the entire refinement procedure run from the start with the opposite enantiomorphs via the empirical absorption correction are $R = 0.035$ and $R_w = 0.037$ (white) and $R = 0.032$ and $R_w = 0.033$ (red), ruling out those possibilities with a much

TABLE 1
Atomic Coordinates, Anisotropic Temperature Factors ($T = \exp[-\{(h^2 + k^2 + hk)\beta_{11} + l^2\beta_{33}\}]$), the Isotropic Equivalent B_{eq} , Isotropic Extinction g , and Interatomic Distances (e.s.d.'s in Parentheses)

	White		Red	
	Zn	O	Zn	O
x	2/3	2/3	2/3	2/3
y	1/3	1/3	1/3	1/3
z	0	0.619(3)	0	0.618(3)
β_{11}	0.0201(3)	0.020(1)	0.0200(3)	0.020(1)
β_{33}	0.00625(4)	0.0059(2)	0.00626(3)	0.0063(2)
B_{eq}	0.651(5)	0.64(3)	0.648(5)	0.65(3)
$g \times 10^2$		0.39(5)		0.21(4)
Zn–O ^a		1.986(2)		1.986(2)
Zn–O' ($\times 3$) ^a		1.9745(5)		1.9746(5)

^a Symmetry codes; Zn, (x, y, z); O, ($x, y, z - 1$); O', ($y, x, z - 1/2$).

higher significance than the most critical 0.005 level in Hamilton's test (13).

Chemical analysis on the red ZnO we have prepared indicated approximately 0.003% excess Zn, a typical value similar in magnitude to previous chemical analyses (3–7).

The various parameters listed in Table 1¹ exhibit very similar values for white and red crystals. The difference Fourier sections for both crystals (Fig. 1) show no significant characteristics of $>1e/\text{\AA}^3$ other than those near the special positions. Likewise, the $F' - F$ and $D' - D$ ($D = F_o - F_c$) difference Fourier sections synthesized from the structure factor data of the white and red (with primes) samples (for 262 common reflections, $R_{(F'-F)} = 0.017$, $R_{(D'-D)} = 0.008$) also lack large residuals except for those seen at the vicinity of the Zn atoms. Slight discrepancies of the temperature factors along with the other parameters as well as the accumulation of various errors are probable causes of these deformations. A check of the D values showed F_o vs F_c misfits of over 4% in the low-angle $00k$ reflections and also in reflections such as $1,0,\pm 12$ or $1,1,\pm 12$ in the white data. Omission of these data in the calculations of the white data decreased the residual peak heights, though the features persisted. These results suggest the possibility of uncorrected anisotropic effects from particular orientations of defects or the crystal mosaic structure in the white sample. Thus, the empirical absorption and isotropic extinction corrections in the initial data reduction

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may have fared better for the red sample. In both the red and white samples, the broad diffraction profiles tend to be even wider in the ω than in the $2\theta-\omega$ scans, indicating a wide angular distribution in the orientation of the crystallites. We believe, however that these problems do not alter the prime conclusions drawn below.

The absence of peaks indicative of bonding electrons along the Zn-O vector is consistent with the ionic character for this substance. Cell constants did not show significant differences between red and white ZnO. Furthermore, accurate assessment of electron density residuals confirms the results of chemical analyses that concentration of Zn interstitials in red ZnO is much too low to be detectable in a difference Fourier map.

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