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New High-Pressure Polymorph of Zinc Oxide

Abstract. Zinc oxide exists in a sodium chloride structure form in the 100-kilobar pressure range. The cell edge of the high-pressure form is 4.280 A, the theoretical density is 6.912, and the enthalpy of transition is 785 cal/mole.

Zinc oxide (zincite) has a slightly distorted hexagonal wurtzite structure, and Bragg and Darbyshire (*1*) have claimed, after electron diffraction of thin films, that it can also exist in a cubic modification with the sphalerite structure. From a qualitative consideration of the effects of high pressures on ionic radii, zinc oxide, if subjected to high pressures, should invert to a NaCl structure. This polymorphic transition would produce a primary change in coordination number from four in the wurtzite structure to six in the NaCl structure.

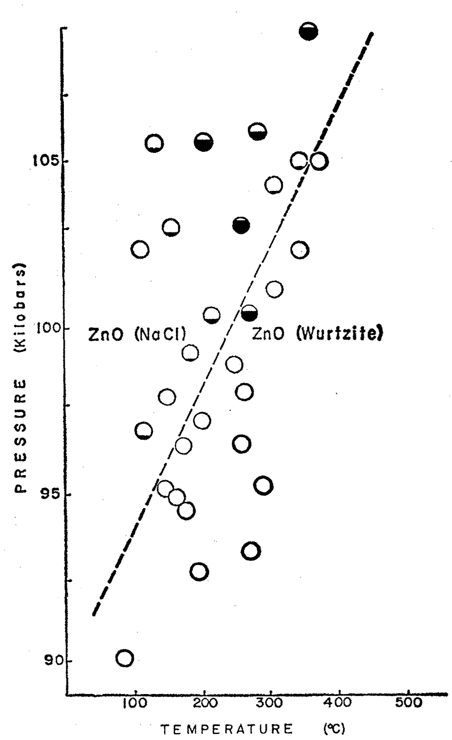

Fig. 1. Plot showing the *P-T* conditions for the formation of the NaCl form of ZnO. The dotted line is the approximate equilibrium curve.

We have synthesized a high-pressure polymorph of zinc oxide with the cubic NaCl structure.

The apparatus used and its accuracy, reproducibility, and limitations are essentially those described by Dachille and Roy (*2*), who used Bridgman (*3*) compound anvils. A Rene alloy anvil with a conical insert of grade 886 carboloy with 3/16-inch effective surface diameter was used for most of the runs. A small drop of saturated ammonium chloride solution was placed on the sample as a catalyst before the pelleted sample was covered with platinum–10-percent rhodium disks and placed between the anvils. The variation in recorded pressure during a single run was not more than ±6.5 kbar, as indicated on the Foxboro pressure controller.

In several runs above about 100 kbar a new form of ZnO appeared, and a univariant equilibrium curve between the two polymorphs based on such runs is presented in Fig. 1.

The new phase is identified and characterized by its x-ray powder pattern, which contains the distinctive reflections shown in Table 1. No higher angle peaks could be detected in a diffractometer pattern. The a_o for the NaCl structure phase is 4.280 A, which gives a theoretical density of 6.912, whereas the density for the zincite structure is 5.680. Conversion could be effected only with ammonium chloride as a catalyst. Other substances, including distilled water and 0.1*N* sodium carbonate solution, produced no detectable conversion even at pressures well above the equilibrium curve. It would appear that the catalytic action of the ammonium chloride comes from formation of zinc-ammonia complexes. The rate of conversion appears to be very slow and usually a period of 36 to 48 hours is required to produce an appreciable amount of the new phase. Even with long runs the yield is only 30 percent. So far the new phase has not been prepared free from contamination by zincite.

The effect of shear on the phase transition was also studied, by the technique described by Dachille and Roy (*4*), but no conversion could be detected. However, with shear under pressures of about 100 kbar only short runs without catalyst could be made.

Table 1. Distinctive reflections in x-ray powder pattern of new zinc oxide phase.

hkl	*d* (A)	I/I_o
111	2.479	60
200	2.140	100
222	1.5135	40

Sample extrusion and anvil failure under the high stresses produced were the controlling factors.

The high-pressure polymorph showed no tendency to revert to the wurtzite form even after it had stood for several weeks at room temperature. However, the high-pressure form does revert to the wurtzite structure at as low as 120°C (in 3 weeks). This may suggest that the inability to obtain the NaCl-phase pure may be due to failure of quenching.

The value of dP/dT as obtained from the equilibrium curve gives a value of 42.5 atm/°C, yielding a ΔH of transition from the Clapeyron relation of 785 cal/mole at 25°C (*5*).

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A Gene in Drosophila That Produces a New Chromosomal Banding Pattern

Abstract. A change in the banding pattern of the distal end of the third chromosome in *Drosophila pseudoobscura* has been found. It appears to be produced by homozygosis for a recessive gene, which is called "salivary" (sal) in this report.

In the course of an experiment dealing with inversion polymorphism in *Drosophila pseudoobscura* (*1*), a new banding pattern, at the distal end of the third chromosome, was observed by one of us (L.L.) (Fig. 1). It was