X-Ray Diffraction Study of ZnF$_2$ at Pressures up to 130 kbar at 25 and 300°

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Abstract

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X-Ray Diffraction Study of ZnF_2 at Pressures up to 130 kbar at 25 and 300°

A study has been carried out of the effect of high pressure up to 130 kbar on the structure of ZnF_2 at 25 and 300°. It is known that S. S. Kabalkina and S. V. Popova discovered a rhombic modification of ZnF_2 (^{1}), isostructural with α-PbO_2 (^{2}), after the action of pressure $P > 50$ kbar and a high temperature of $\sim 1700°$. The new phase proved to be metastable under ordinary conditions. Metastable phases of α-PbO_2 were also found in MnF_2 (^{1,3}) and TiO_2 (^{4,5}). In contrast to ZnF_2 and TiO_2, this phase in MnF_2 can be obtained at considerably lower pressures, $P > 20$ kbar, and at room temperature.

As has already been noted earlier (^{1,3}), investigations of MnF_2, ZnF_2 were undertaken with the aim of detecting a phase transition from the rutile structural type to the fluorite type. At present it is evident that the negative results of the experiments did not exclude the possibility of the existence of a fluorite phase under conditions of high pressure and temperature; they showed only that the fluorite phase (if it exists) had not yet been preserved under ordinary conditions.

Naturally, in order to obtain an exhaustive answer to the question of the possibility of the existence of cubic modifications of MnF_2, ZnF_2, TiO_2, etc., it is necessary to carry out an x-ray diffraction study of the structure of these substances directly under conditions of high pressure and temperature. A study of the structure of MnF_2 at high pressures and room temperature (^{6}) showed that at $P > 20$–30 kbar the initial rutile phase undergoes a reversible polymorphic transition, and the data obtained make it possible to suppose that the high-pressure phase of MnF_2 has a distorted structure of the CaF_2 type, close to the structure of tetragonal ZrO_2; the metastable α-PbO_2 phase is formed after or during pressure release. From a personal communication of Prof. Jamieson it became known that he succeeded in detecting, at high pressure, the transformation of the initial rutile phase of ZnF_2 into the cubic CaF_2 type, partial at lower pressures and complete at higher ones; the α-PbO_2 phase was obtained after pressure release. These data have not yet been published, and therefore the specific conditions for the existence of the fluorite phase of ZnF_2 are not known.

The x-ray diffraction study of ZnF_2 was carried out by us in a chamber whose

Fig. 1. Schematic section of the high-pressure chamber.

Figure 1: Fig. 1. Schematic section of the high-pressure chamber.

design makes it possible to obtain Debye photographs of crystalline substances that are simultaneously under conditions of high pressure up to ~ 130 kbar and high temperature up to 300°.*

Figure 1 schematically shows a cross section of the chamber. Its main part is a tablet **1** of amorphous boron with a channel for the sample, placed between two anvils **2** of hard alloy VK-6. The anvils are inserted into a steel ring **3**, in which there is an opening for the diaphragm **4**, a slit for the exit of diffracted rays, and two grooves for the heating spiral **5** of nichrome with asbestos insulation. The temperature of the chamber is stabilized with the aid of an MRPShPr-54 thermoregulator, into whose circuit is connected a chromel–alumel thermocouple recording the temperature in the ring. To reduce heat loss, between the chamber and the press there are heat-insulating asbestos gaskets 6. To prevent heating of the press, water cooling is used. The semicylindrical cassette 7 also has water cooling 8, which protects the film from heating. The pressure in the chamber is produced by means of a miniature hydraulic press with a force of 20 tons.

To estimate the possible temperature drop in the ring and in the specimen, special experiments were carried out. A chromel–alumel thermocouple, made from wire of 0.05 mm cross section, was placed in a precompressed boron pellet so that its junction, 0.15 mm in diameter, was at the center of the channel surrounded by the substance under study. Comparing the readings of the thermocouples, we established that at 300° the temperature inside the pellet may differ from the temperature of the ring by no more than 5°.

Fig. 1. Schematic section of the high-pressure chamber. 1 –pellet of amorphous boron with a channel for the specimen; 2 –anvils of hard alloy; 3 –steel ring; 4 –diaphragm for the entrance of X-rays; 5 –heating coil of nichrome; 6 –heat-insulating gaskets; 7 –cassette with film; 8 –water cooling; 9 –opening for introducing the thermocouple.

Calibration of the chamber with respect to pressure was carried out radiographically from the compressibility of NaCl. In order not to complicate the diffraction pattern, ZnF_2 and NaCl were photographed separately. Naturally, the accuracy of determining P in individual experiments was thereby reduced and was ~ ±5 kbar. The compressibility of NaCl was estimated from Bridgman' s data (9).

A detailed X-ray study of ZnF_2 was carried out at room temperature and high

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* This chamber differs little from the chamber used by us for studies at room temperature (7); it is also close to Jamieson' s chamber (8).

pressure up to ~ 130 kbar; as a result, a reversible phase transition from rutile to a monoclinic phase was found, apparently isostructural with the monoclinic modification of ZrO_2—baddeleyite (^{10}). The onset of the transition at 70-80 kbar can be observed from a noticeable change in the ZnF_2 radiographs: weakening of the rutile line (101), broadening of (211), and the appearance of a "new" line with $d = 2.76$ Å, corresponding to the $(11\bar{1})$ reflection in "baddeleyite." At $P \simeq 110$ kbar the transition is completely completed, and the radiographs obtained under these conditions apparently correspond to the monoclinic modification of ZnF_2.

Table 1 gives data characterizing the new phase. The interplanar spacings d_{calc} were determined for a unit cell with parameters: $a = 5.29$ Å, $b = 4.96$ Å, $c = 5.05$ Å, $\beta = 79°23'$, $Z = 4$. In calculating the intensities of the (hkl) reflections, it was assumed that in the monoclinic phases ZnF_2 and ZrO_2 the atoms occupy identical positions in the unit cell (^{10}). Some discrepancy between the experimental data and the calculated values can apparently be attributed to the difference between the specified and true values of the coordinates of the Zn and F atoms. The density of the new phase, $\rho = 5.27$ g/cm^3, is approximately 7% greater than that of rutile (without taking its compressibility into account). Experiments carried out at room temperature, after removal of the pressure, gave radiographs of pure rutile.

An X-ray study at high pressure and a temperature of 300° made it possible to discover a cubic phase of ZnF_2 with a CaF_2-type structure at $P = 70$–80 kbar. We succeeded five times in recording the fluorite-

phase under these conditions. In 4 experiments the X-ray patterns contained only lines of the cubic phase; in one, a two-phase pattern with lines of rutile and fluorite was obtained, which made it possible to estimate the pure volume jump in the transition from the first modification to the second, $\Delta v/v_0 \simeq 9\%$:

hkl	111	200	220	311
$I_{obs.}$	strong	very weak	medium	medium
$d_{obs.}$, Å	2.841	2.456	1.741	1.481
a, Å	4.921	4.912	4.924	4.912

$$a_{avg} = 4.917 \text{ Å}, \qquad \rho = 5.77 \text{ g/cm}^3$$

In all 5 experiments the X-ray patterns after pressure release at room temperature corresponded to rutile with a small admixture of the α-PbO_2 phase. A scheme of the X-ray patterns of the different phases of ZnF_2 is given in Fig. 2. It should be recalled that in work (^{1}) X-ray patterns of α-PbO_2 with an admixture of rutile were obtained after ZnF_2 had been under conditions $P > 50$ kbar and $T > 1500°$, under which, apparently, the fluorite phase is the equilibrium one.

It is natural to suppose that the α-PbO_2 phase is an intermediate stage in the transformation of fluorite into rutile*, which can be retained under ordinary conditions as a metastable modification. Evidently, it is considerably easier to retain the α-PbO_2 phase after high-temperature experiments than after low-temperature experiments. In order to prove rigorously the validity of the hypothesis put forward, a careful X-ray investigation of the fluorite → rutile transition should be carried out with successive lowering of P and T. It has been established that in the direct rutile → fluorite transition α-PbO_2 is not obtained. Moreover, under the action of high pressure the α-PbO_2 phase in the case of ZnF_2, as also in MnF_2 (6), transforms into rutile. The reason for the difference in the behavior of ZnF_2 in the direct and reverse rutile—fluorite transition remains unclear. It is possible that, upon pressure release, shear stresses arise which promote the appearance of the α-PbO_2 phase.

Table 1

hkl	*I*, calc.	*I*, obs.	*d*, Å calc.	*d*, Å obs.	*hkl*	*I*, calc.	*I*, obs.	*d*, Å calc.	*d*, Å obs.
111	100	strong	3.10	3.12	220	61		1.79	
$1\bar{1}1$	84	strong	2.75	2.76	221	9	very weak	1.76	1.79
200	14		2.60		022	42		1.75	
002	23	medium	2.48	2.48	300	3		1.73	
020	8	very diffuse	2.48		122	1	medium	1.73	1.71
102	20		2.42		310	2		1.69	
211	1		2.23		$2\bar{0}2$	33		1.65	1.63
112	25	very weak	2.17	2.15	$2\bar{2}1$	15	weak	1.62	
121	17		2.10		122	34		1.60	
$1\bar{0}2$	1		2.09		302	1	very weak	1.56	
202	46		1.93		222	13		1.56	1.57
$1\bar{2}1$	12	moderately strong	1.98	1.98	131	29		1.53	
$2\bar{1}1$	16		1.97		$1\bar{3}1$	14	weak	1.48	1.52
$1\bar{1}2$	1		1.93		$2\bar{2}2$	15	medium	1.38	1.40
					$3\bar{0}2$	7	weak	1.31	1.32

In one of the recent papers (5) α-PbO_2 is called a distorted fluorite phase. Indeed, if in the unit cell of α-PbO_2 the zinc atom is assigned coordinates $x = 0$, $y = z = 1/4$, and fluorine $x = 1/4$, $y = z = 1/2$, then we obtain a rhombically distorted structure of the CaF_2 type, representing, in the figurative expression of N. V. Belov, a three-dimensional chess—

* The results obtained for MnF_2 (6) make it possible to suppose that α-PbO_2 is also an intermediate for the distorted-fluorite → rutile transitions.

···board [11], in which the Zn atoms occupy the centers of rectangular parallelepipeds, rather than regular cubes as in CaF_2. In fact, in the α-PbO_2 structure the zinc atoms are somewhat displaced from the centers of the oblique-angled parallelepipeds formed by the fluorine atoms. Thus, in the $CaF_2 \to \alpha$-PbO_2 transition the fluorine atoms move away from the cube vertices and Zn is displaced from its center.

Fig. 2. Scheme of the X-ray diffraction patterns of ZnF_2 at different pressures and temperatures.
a—$P = 1$ bar, $T = 25°$, rutile phase;
b—$P = 110$ kbar, $T = 25°$, "baddeleyite" phase;
v—$P = 80$ kbar, $T = 300°$, "fluorite" phase;
g—$P = 1$ bar, $T = 25°$ (after removal of high pressure and temperature), rutile phases with an admixture of the α-PbO_2 phase; the lines of the α-PbO_2 phase are marked with a dotted line. The cross marks the exit of the primary beam in the photograph.

Table 2

Substance	Phase	Unit-cell parameters	ρ, g/cm^3	Zn—F distance
ZnF_2	Rutile ($P = 1$ bar, 25°)	$a = 4.711$ Å, $c = 3.132$ Å, $Z = 2$	4.94	Four 2.07 Å
ZnF_2	Baddeleyite ($P = 110$ kbar, 25°)	$a = 5.29$ Å, $b = 4.96$ Å, $c = 5.05$ Å, $\beta = 79°23'$, $Z = 4$	5.27	Two 2.01 Å
ZnF_2	Fluorite ($P = 80$ kbar, 300°)	$a = 4.92$ Å, $Z = 4$	5.77	Eight 2.13 Å
ZnF_2	α-PbO_2 ($P = 1$ bar, 25°)	$a = 4.683$ Å, $b = 5.658$ Å, $c = 5.166$ Å, $Z = 4$	5.01	Four 2.06 Å, two 2.03 Å
ZrO_2	Baddeleyite	$a = 5.169$ Å, $b = 5.232$ Å, $c = 5.341$ Å, $\beta = 80°45'$, $Z = 4$	5.826	

Substance	Phase	Unit-cell parameters	ρ, g/cm^3	Zn—F distance
ZrO_2	Tetragonal	$a =$ 5.15 Å, $c =$ 5.27 Å, $Z =$ 4	5.86	
ZrO_2	Fluorite	$a =$ 5.07 Å, $Z =$ 4	6.28	

Table 2 collects data characterizing the ZnF_2 phases—rutile, baddeleyite, fluorite, and α-PbO_2. In complete agreement with Goldschmidt' s data on the effect of coordination number on the magnitude of the interatomic distance in ionic crystals, the Zn—F distance in the CaF_2 phase is about 3% greater than in rutile and α-PbO_2. For comparison, tabulated data for the analogous phases of ZrO_2 are also given there.

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Note: Figure translations are in progress. See original paper for figures.