PHASE TRANSITION IN ZINC AND MANGANESE FLUORIDES AT HIGH PRESSURES AND TEMPERATURES

1963

SovietRxiv

Abstract

Full Text

CRYSTALLOGRAPHY

S. S. Kabalkina, S. V. Popova

PHASE TRANSITION IN ZINC AND MANGANESE FLUORIDES AT HIGH PRESSURES AND TEMPERATURES

(Presented by Academician N. V. Belov, 27 IV 1963)

A study has been made of the stability of structural analogs of rutile: magnesium, zinc, and manganese fluorides at high pressures and temperatures. It is known that MgF_2 and ZnF_2 lie at the boundary of a morphotropic transformation between fluorides with the rutile structure and the fluorite structure in the morphotropic series: BeF_2–MgF_2–CaF_2–SrF_2, ZnF_2–CdF_2. It may be assumed that at high pressure MgF_2, ZnF_2, and MnF_2 will have fluorite structures. The latter also follows from the fact that the ratio of ionic radii in ZnF_2 and MnF_2, according to Goldschmidt' s criterion, is close to the upper stability limit of the rutile structure.

In the present work we attempted to obtain new modifications of MgF_2, ZnF_2, and MnF_2 under conditions of high pressure, 30-140 kbar,* and temperatures up to 1700°. The substance after the experiment was analyzed by x-ray diffraction. It was established that MgF_2 under these conditions retains the rutile structure. Investigation of ZnF_2 made it possible to detect a new phase, ZnF_2 II, isostructural with α-PbO_2 (2), which arises at $p = 50$ kbar. The transition ZnF_2 I → ZnF_2 II is accompanied by a change in the color of the substance–from white it becomes dark gray. Table 1 gives the cell parameters, line intensities, and interplanar spacings of the new phase ZnF_2 II; according to x-ray data its density is 5.01 g/cm^3, the corresponding density value for ZnF_2 I being 4.94 g/cm^3. Thus, in the phase transition ZnF_2 I → ZnF_2 II the density increases by 1.4%. It should be noted that lines of ZnF_2 I are present on the x-ray diffraction patterns of the new phase ZnF_2 II. From the ratio of the intensities of the lines of the two phases it follows that the amount of the old phase in the sample after the experiment does not exceed 30%. Annealing it for 2 hours at a temperature of 400° leads to the reverse transition

Table 1

hkl	*I*	*d* calc.	*d* measured	*hkl*	*I*	*d* calc.	*d* measured
110	69	3.608	3.607	113	12	1.554	1.555
111	100	2.958	2.953	222	7	1.479	1.469

hkl	I	d calc.	d measured	hkl	I	d calc.	d measured
020	5	2.829	2.843	311	21	1.445	1.446
002	9	2.583	2.590	040	5	1.414	1.418
021	25	2.481	2.481	041	6	1.364	1.371
200	5	2.341	2.341	312	4	1.300	1.297
102	12	2.262	2.265	223	6	1.245	1.244
121	20	2.192	2.192	330	6	1.202	1.204
112	10	2.100	2.093	241	5	1.179	1.181
220	9	1.804	1.801	331	5	1.171	1.171
130	13	1.749	1.751	204	8	1.131	1.130
202	28	1.735	2.735	332	6	1.090	1.093
221	50	1.703	1.703	420	4	1.082	1.080

$$a = 4.683 \pm 0.001\ \text{Å}, \quad b = 5.658 \pm 0.001\ \text{Å}, \quad c = 5.166 \pm 0.001\ \text{Å}$$

* The pressure values were taken according to the Kennedy and LaMori scale (^{1}).

To the article by S. S. Kabalkina and S. V. Popova

Fig. 1. Three Debyegrams obtained with the RKU-114 camera using copper filtered radiation. **a**–initial ZnF_2 I (rutile); **b**–ZnF_2 II (α-PbO_2 phase), obtained at $P = 120$ kbar and $t = 1300°$; weak lines of the initial phase are observed in the roentgenogram; **c**–ZnF_2 I, obtained by annealing ZnF_2 II.

ZnF_2 II → ZnF_2 I; the X-ray pattern of the annealed product coincides completely with the X-ray pattern of the initial ZnF_2 I (see Fig. 1). Thus it has been proved that the ZnF_2 II phase, obtained at high pressures, is metastable under ordinary conditions.

It is known that Azzaria and Dachille (^{3}) obtained a new modification, MnF_2 II, at a pressure of about 20 kbar and a temperature of ~200°, also isostructural with α-PbO_2. Our attempts to obtain MnF_2 with the fluorite structure at higher pressure and temperature were unsuccessful. X-ray patterns of the product obtained showed that the MnF_2 II phase is stable up to $p = 140$ kbar and 1700°. However, in some experiments at the maximum pressure we observed in the Debyegrams a number of additional lines that could not be indexed in the α-PbO_2 structure, which apparently indicates a new transition at higher pressures. It is known

Fig. 2. Arrangement of filled octahedra of fluorine atoms (view in the direction of the a axis) for ZnF_2 II (A) and MnF_2 II (B); the lengths of the corresponding edges are indicated.

also that Roy et al. (^{4}) obtained, at $p = 13$ kbar and 300°, a transition of the rutile modification of PbO_2 into a new phase with the α-PbO_2 structure. Thus,

Fig. 2. Arrangement of filled octahedra of fluorine atoms (view in the direction of the a axis) for ZnF_2 II (A) and MnF_2 II (B); the lengths of the corresponding edges are indicated

Figure 1: Fig. 2. Arrangement of filled octahedra of fluorine atoms (view in the direction of the a axis) for ZnF_2 II (A) and MnF_2 II (B); the lengths of the corresponding edges are indicated

three different compounds with the initial rutile structure—PbO_2, MnF_2, and ZnF_2—acquire the α-PbO_2 structure at high pressure. In the transition of the rutile modification to α-PbO_2, the type of packing (dense hexagonal) and the coordination number are retained; only the motif of the arrangement of cations changes. In rutile, the Pb(Mn, Zn) atoms occupy half of the octahedral voids, according to the motif—a row of occupied, a row of empty; the corresponding chains of octahedra are rectilinear; in α-PbO_2, zigzag chains of occupied and empty octahedra alternate ([2],[5]).

It should be noted that the α-PbO_2 structure was assigned to the new modifications MnF_2 II and ZnF_2 II as a result of unambiguous indexing of Debyegrams on the basis of a primitive rhombic cell with reflections corresponding to the space group $D_{2h}^{14} = Pbcn$. To confirm the validity of this, we carried out a complete analysis of the structures of ZnF_2 II and MnF_2 II using the data obtained from the Debyegrams. In doing so, the intensities of the (hkl) reflections were used (for each compound there were approximately 40 reflections), estimated with the aid of blackening standards. The isostructurality of MnF_2 II and ZnF_2 II with α-PbO_2 leads to the following arrangement of atoms in the structure: Zn (Mn) $0y{}^1/_4$, $0\bar{y}{}^3/_4$, ${}^1/_2\ {}^1/_2{+}y{}^1/_4$, ${}^1/_2\ {}^1/_2{-}y{}^3/_4$; F xyz, ${}^1/_2{-}x\ {}^1/_2{-}y\ {}^1/_2{+}z$, ${}^1/_2{+}x\ {}^1/_2{-}yz$, $x\bar{y}\ {}^1/_2{-}z$, $x\bar{y}z$, ${}^1/_2{+}x\ {}^1/_2{+}y\ {}^1/_2{-}z$, ${}^1/_2{-}x\ {}^1/_2{+}yz$, $x\bar{y}\ {}^1/_2{+}z$.

Thus, the problem reduces to determining four parameters: one parameter corresponding to zinc (manganese), and three parameters of fluorine. The presence in the group D_{2h}^{14} of three glide planes makes it possible to determine the parameters comparatively simply by means of three Harker section lines through a three-dimensional Patterson synthesis (along the principal directions of the cell). Summation of the F^2-series was carried out with the aid of 3° strips (for 120 points along each period of the cell).

The atomic coordinates obtained from the three-dimensional synthesis are given in Table 2.

To refine the results obtained, we used the least-squares method, whose application is especially useful for solving structural problems in cases where there is not a sufficient amount of experimental data to ensure convergence of the series. By this method the atomic coordinates were refined (Table 2) and the temperature corrections (B and U) were determined in both structures. All computational operations were performed on an electronic computer. When the experimental F_{hkl} were compared with the calculated ones, the discrepancy factor R proved to be 0.21 for MnF_2 II and 0.26 for ZnF_2 II.

Table 2

Compound	Atom	F^2-series x	F^2-series y	F^2-series z	Least-squares method x	Least-squares method y	Least-squares method z	B	U
ZnF_2	Zn	0	0,162	0,25	0	0,163	0,25	1,57	–0,15
ZnF_2	F	0,23	0,42	0,39	0,266	0,403	0,428	–	1,64
MnF_2	Mn	0	0,15	0,25	0	0,165	0,25	1,73	–0,40
MnF_2	F	0,25	0,42	0,41	0,266	0,390	0,421	–	2,59
α-PbO_2(2)	Pb	0	0,178	0,25					
α-PbO_2	O	0,26	0,43	0,44					

The data obtained made it possible to estimate the distances between atoms in the structures considered: in ZnF_2 II the Zn–F distances are from 2.03 to 2.06 Å, and in MnF_2 II the Mn–F distances are from 2.07 to 2.17 Å. The sum of the corresponding ionic radii is 2.16 Å in ZnF_2 and 2.24 Å in MnF_2. Thus, in both cases a covalent component is superimposed on the ionic bond. The length of the common edge of the octahedron is 2.56 Å in ZnF_2 II and 2.78 Å in MnF_2 II (in α-PbO_2(2), 2.58 Å).

In conclusion, the authors express their deep gratitude to Corresponding Member of the Academy of Sciences of the USSR L. F. Vereshchagin for his attention to and discussion of this work, as well as to Yu. T. Struchkov for assistance in carrying out the least-squares calculations on an electronic computer, and to N. S. Tamm for providing samples for the investigation.

Institute of High Pressure Physics
Academy of Sciences of the USSR

Received
19 IV 1963

REFERENCES

1. G. C. Kennedy, P. N. La Mori, *Progress in Very High Pressure Res.*, N.Y. –London, 1961, p. 304.
2. A. I. Zaslavskii, Yu. D. Kondrat'ev, S. S. Stolkachev, DAN, **75**, 559 (1950).
3. L. M. Azzaria, Frank Dachille, *J. Phys. Chem.*, **65**, 889 (1961).

4. W. B. White, F. Dachille, R. Roy, *J. Am. Ceram. Soc.*, **44**, 4 (1961).
5. N. V. Belov, *Structure of Ionic Crystals and Metallic Phases*, Publishing House of the Academy of Sciences of the USSR, 1947.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.