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Conditions for the Formation and Existence of a MnF_2 Phase with α-PbO_2 Structure

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X-ray studies show that isothermal lowering of pressure from 70 kbars to atmospheric pressure induces in MnF_2 with initial rutile structure the following structural transformations: distorted fluorite → fluorite → α-PbO_2 (at 300° and 400°C) or distorted fluorite → α-PbO_2 (at 25°C). Reapplication of pressure on the same sample induces the transformations in reverse order: α-PbO_2 → fluorite → distorted fluorite (at 300° and 400°C) or α-PbO_2 → distorted fluorite (at 25°C). The formation and continued existence of the α-PbO_2 phase under these conditions depend on shear stresses that exist in the sample during the removal and reincrease of pressure.

STRUCTURE of the α-PbO_2 type, which was predicted by Pauling and Sturdivant[1] in 1928, was first observed and identified as one of the modifications of PbO_2 by A. I. Zaslavskiĭ et al.[2] At the present time we know of several AX_2 compounds and their ABX_4 homotypes[3] 1) that crystallize in this structure.

High pressures and temperatures have been used to produce synthetically the α-PbO_2 type modifications,2) which are metastable under normal conditions, of several compounds having initial rutile structure: PbO_2,[4,5] MnF_2,[5-7] ZnF_2,[5,7] TiO_2,[5,8,9] and $InSbO_4$.[5] The average increase of density as compared with the rutile modification is 1–2%, and is brought about through compression of the distorted hexagonal packing of anions that characterizes these structural types.

Among the aforementioned compounds the polymorphism of MnF_2 has been studied most completely. In our earlier work[10,11] we investigated the effect of high pressures on the crystalline structure of manganous fluoride at temperatures from 25° to 400°C. With the increase of P the following sequences of structural transformations are observed: for $T > 200°C$, rutile → fluorite → distorted fluorite; for $T < 200°C$, rutile → distorted fluorite (Fig. 1). After the reduction of the pressure and temperature the samples possessed α-PbO_2 structure. It was also found that when the metastable α-PbO_2 phase3) is placed in a high-pressure vessel for x-ray studies (in a boron pellet) and is subjected to sufficiently high pressure, the α-PbO_2 → rutile transformation occurs at $P < 30$ kbar. This is the basis for the hypothesis that the P-T diagram will contain no definite region for the α-PbO_2 phase and that the appearance of this phase is promoted by shear stresses that arise in the chamber when the pressure is lowered.

In further study of the conditions permitting the α-PbO_2 phase, we performed a detailed investigation of the crystal structure of MnF_2 when the pressure upon it was reduced from 70 kbar to atmospheric pressure at 400°, 300°, and 25°C, i.e., we investigated its P-T diagram for the decreasing leg of the pressure cycle. We used an externally heated high-pressure x-ray camera with which Debye-Scherrer powder patterns are obtained directly while the samples of materials are being subjected to high pressures and temperatures.[12] To the samples of MnF_2 we added NaCl, which served as an internal pressure gauge. We computed P from the change of the NaCl lattice constant as a function of pressure and temperature, using the semiempirical equation of state calculated by Decker.[13] The pressure error was $\sim\pm 5\%$, which was determined from the error in measuring the NaCl lattice constant. The temperature error was ±10°. The MnF_2 samples with initial rutile structure were subjected to 60–70 kbar at 400°, 300°, and 25°C during 5–10 minutes. X-ray photographs were then obtained following successive isothermal reductions of the pressure. The following phase transformations were observed: distorted fluorite → fluorite → α-PbO_2 at 300° and 400°C and distorted fluorite → α-PbO_2 at 25°C. The results are shown in Fig. 2a. From these data we determine the regions of the different phases under the given conditions. The α-PbO_2 phase appears when the pressure is reduced to 10 ± 2 kbar. At atmospheric pressure and 400°C this phase is completely annealed out in 4 hours and is transformed into the rutile modification; at 300° during the same period of time the α-PbO_2 phase does not change but remains as a metastable state.

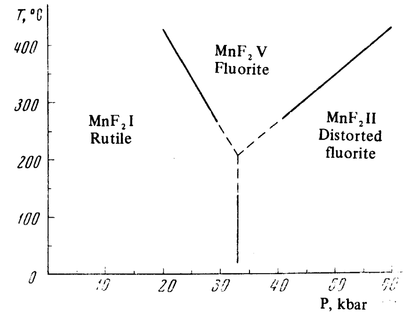

FIG. 1. Phase diagram of MnF_2 [11].

To investigate the possibility of a transformation from α-PbO_2 to the fluorite structure, the α-PbO_2 phase produced by pressure reduction was again subjected to high pressure in the same pellet. The results, shown in Fig. 2b, indicate a direct transformation from α-PbO_2

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1) The wolframite structure that also characterizes some ABX_4 compounds is an ordered homotype of α-PbO_2 structure.

2) Modifications with α-PbO_2 structures will be called, more briefly, the α-PbO_2 phase.

3) The metastable α-PbO_2 phase was produced in advance in a high-pressure vessel that was large enough[7] to furnish material for an entire series of studies.

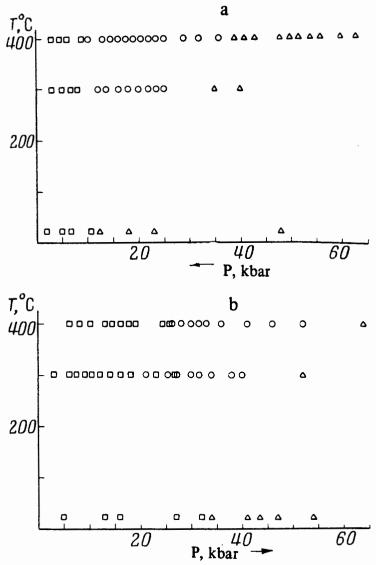

FIG. 2. Regions of the different MnF_2 phases: a—during pressure decrease in the first cycle; b—during reincrease of pressure in the second cycle. Symbols: □—α-PbO phase, O—fluorite phase, Δ—distorted fluorite phase.

to fluorite at 25 ± 3 kbar. A comparison of Fig. 2, a and b, with the P-T diagram for pressure increase[11] indicates the hysteresis of the phase transformations: ~15 kbar for α-$PbO_2 \rightleftarrows$ fluorite (300° and 400°C) and ~20 kbar for fluorite $\rightleftarrows$ distorted fluorite (400°C).

We have thus proved the existence of the reversible polymorphic transformations α-$PbO_2 \rightleftarrows$ fluorite and α-$PbO_2 \rightleftarrows$ distorted fluorite. At first glance this result disproves our earlier hypothesis[10] that the P-T diagram of MnF_2 contains no region for a stable phase with α-PbO_2 structure. We therefore repeated the x-ray study of this modification under high pressure at 25° and 300°C, after its production in a vessel of large volume (at 50 kbar and 600°C).[4)] For this purpose the α-PbO_2 phase was imbedded in a fresh boron pellet that exhibited plastic flow under the applied pressure. The results agreed with those of [10]: under increasing pressure we observed the polymorphic transformations α-$PbO_2 \rightarrow$ rutile $\rightarrow$ fluorite (at 300°C) and α-$PbO_2 \rightarrow$ rutile $\rightarrow$ distorted fluorite (at 25°C). It must be kept in mind that the transformations α-$PbO_2 \rightleftarrows$ fluorite and α-$PbO_2 \rightleftarrows$ distorted fluorite in manganous fluoride were observed only when the boron pellet containing the sample was subjected to a reincrease of pressure in the second cycle or decreasing pressure in the first cycle. Under these conditions the medium that transmitted the pressure (the boron pellet) becomes less plastic and the pressures are nonhydrostatic; thus shear stresses are generated in the sample. On this basis we conclude that the shear components of the stresses promote the appearance of the α-PbO_2 phase during pressure decrease and its persistence under reloading until the α-$PbO_2 \rightarrow$ fluorite transformation occurs. The regions of the different MnF_2 modifications should appear in a P-T-Y diagram. However, we cannot quantitatively evaluate the shears Y acting upon the sample in the high pressure vessel. The α-PbO_2 phase appears only when $Y \neq 0$ (Fig. 2, a and b).

We also know that the α-PbO_2 phase has been produced by grinding MnF_2 for several hours in a conventional mortar; here appreciable shearing forces undoubtedly existed.[15] This result provides evidence for the influence of shear stresses on the formation of the α-PbO_2 phase. This becomes clear when we consider the possible mechanism of the rutile $\rightarrow \alpha$-PbO_2 transformation from the point of view of crystal chemistry. A shear-induced deformation can promote the transformation of straight chains of populated octahedra (rutile) into zigzag chains (α-PbO_2). In Buerger's classification [16] this structural transformation is of the deformational type. Also, we have previously shown[12] that the α-PbO_2 structure can be produced by a not very strong distortion of the fluorite structure. Therefore it is reasonable to consider the metastable α-PbO_2 modification as an intermediate stage when the fluorite or fluorite-like phases are transformed into rutile under high pressures.

[4)] The MnF_2 powder was placed in a Pt container; spectroscopically pure graphite was used for heating. The pressure calibration of the vessel was based on the abrupt changes of electric resistance in Bi, Tl, and Ba corresponding to the pressures given for these transitions in[14], i.e., according to a scale based on the compressibility of NaCl; temperatures were measured with an X-A thermocouple inside the high pressure vessel.

[1] L. Pauling and J. H. Sturdivant, Z. Kristallogr. **68**, 239 (1928).

[2] A. I. Zaslavskiĭ, Yu. D. Kondrat'ev, and S. S. Tolkachev, Dokl. Akad. Nauk SSSR **75**, 559 (1950).

[3] A. Magneli and V. O. Marinder Ark. Kemi **21**, 407 (1963).

[4] W. B. White, F. Dachille, and R. Roy, J. Am. Ceram. Soc. **44**, 170 (1961).

[5] K. F. Seifert, Fortschr. Miner. **45**, 214 (1968).

[6] L. M. Azzaria and F. Dachille, J. Phys. Chem. **65**, 889 (1961).

[7] S. S. Kabalkina and S. V. Popova, Dokl. Akad. Nauk SSSR **153**, 1310 (1963) [Sov. Phys. Dokl. **8**, 1141 (1964)].

[8] N. A. Bendeliani, S. V. Popova, and L. F. Vereshchagin, Geokhimiya ,(5), 499 (1966).

[9] R. G. McQueen, J. C. Jamieson, and S. P. Marsh, Science **155**, 1401 (1967).

[10] L. F. Vereshchagin, S. S. Kabalkina, and A. A. Kotilevets, Zh. Eksp. Teor. Fiz. **49**, 1728 (1965) [Sov. Phys. JETP **22**, 1181 (1966)].

[11] S. S. Kabalkina, L. F. Vereshchagin, and L. M. Lityagina, Zh. Eksp. Teor. Fiz. **56**, 1497 (1969) [Sov. Phys. JETP **29**, 1803 (1969)].

[12] S. S. Kabalkina, L. F. Vereshchagin, and L. M. Lityagina, Dokl. Akad. Nauk SSSR **176**, 1044 (1967) [Sov. Phys. Dokl. **12**, 946 (1968)].

[13] D. L. Decker, J. Appl. Phys. **36**, 157 (1965); J. Appl. Phys. **37**, 5012 (1966).

[14] R. J. Jeffery, J. D. Barnett, H. V. Vanfleet, and H. T. Hall, J. Appl. Phys. **37**, 3172 (1966).

[15] F. Dachille and R. Roy, Nature (Lond.) **186**, 34 (1960).

[16] M. J. Buerger, in Phase Transformations in Solids, Wiley, New York, 1951 (Crystallographic Aspects of Phase Transformations, pp. 183–211).

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