JOURNAL OF MATERIALS SCIENCE 27 (1992) 2677–2681

Relative stability of red and black phosphorus at $P<1$ GPa

V. V. BRAZHKIN, A. Ju. ZERR*
Institute of High Pressure Physics, 142092, Troick, Moscow, Russia

Relative stability of red and black phosphorus at $P < 1$ GPa was investigated by rapid and slow cooling from the melt under high pressure and by baro-thermal analysis. The red form was produced from the melt of the black phosphorus. The density of the produced samples of red phosphorus was $\rho = 2.33\ \mathrm{g\,cm^{-3}}$. The existence of a region of stability on the P–T plane for red phosphorus was established. A qualitative phase diagram for phosphorus is presented; the red form is most stable at high temperatures and relatively low pressures. It is necessary to undertake careful investigations at pressures $P < 0.3$ GPa under pure hydrostatic conditions to make quantitative measurements.

1. Introduction

A number of modifications of phosphorus are known, the main ones being white (density $\rho = 1.82\ \mathrm{g\,cm^{-3}}$, melting temperature $T_m = 317.2$ K [1]), red ($\rho = 2.36\ \mathrm{g\,cm^{-3}}$, $T_m = 893$ K [1]) and black ($\rho = 2.69\ \mathrm{g\,cm^{-3}}$ [1], $T_m = 879$ K, on extrapolation to the normal pressure [2]). White phosphorus has a cubic structure and black has the orthorhombic cell type with a space group *Cmca* [3]. Structure data for red phosphorus are contradictory; some authors suppose a monoclinic [4], others cubic [5] symmetry. Because phosphorus is a difficult crystalline molecular compound, it forms amorphous modifications on quenching or precipitation with various degrees of disorder.

On heating, white phosphorus recrystallizes slowly to the red or black form depending on the P–T conditions [6, 7]. The question of relative stability of red and black phosphorus remains open. Irreversible transition from the red to the black form occurs at room temperature at pressure $P = 7.5$ GPa [8], however, in the presence of shear deformations it occurs at $P = 4.0$ GPa [9]. Long *et al.* [10] consider this transformation to be a transition from the metastable state to the stable one. The formation energy of black phosphorus is greater than that of either the red or white forms [11]. It would appear that the more stable form of phosphorus under normal conditions is black. On the other hand, black phosphorus sublimes at $T_s = 823$ K and pressures $P < 0.01$ GPa, but red phosphorus melts at $T_m = 893$ K under atmospheric pressure. Hence, it is possible that a region exists on the P–T diagram, where red phosphorus is more stable than black.

The red crystalline form was prepared previously [4] by slow cooling from the liquid state without indicating any pressure value. Therefore, the type of solid modification generated depends on previous treatment of the phosphorus.

At pressure $P > 1$ GPa, obviously the more stable phase is black phosphorus [10] and the red form does not exist on the stable P–T diagram. In the pressure range $0.01 < P < 1.0$ GPa, the data for the relative stability of the red and black modifications are very contradictory. The purpose of this work was to investigate the red–black phosphorus relative stability at pressures $P < 1.0$ GPa.

2. Experimental procedure

The pressure, created in a toroid-type high-pressure device [12], was graduated according to changes of the electrical resistance of cerium ($P = 0.7$ GPa), bismuth ($P_{\mathrm{I-II}} = 2.54$ GPa and $P_{\mathrm{II-III}} = 2.7$ GPa), the volume anomaly in RbCl ($P = 0.52$ GPa), and the resistivity of manganin. The pressing load was measured using a thensorsensor, which provided the possibility of receiving quantitative data in the pressure range $0.3 < P < 1.0$ GPa.

The initial sample was amorphous red or crystalline black phosphorus powder, pressed in a cylinder 3 mm high with 3 mm diameter. The sample was located in a container prepared from NaCl single crystal (wall thickness 1.5 mm, cover thickness 2.5 mm). The container was surrounded by a graphite heater. A powerful thyristor amplifier, regulated by a linearly increased voltage source, was used as an electrical current supply. The heating velocity was varied in the experiments from 20–100 $\mathrm{K\,min^{-1}}$, with a cooling rate from -10 to $-10^4\ \mathrm{K\,min^{-1}}$ (rapid quenching).

The temperature was measured using chromel–alumel and Pt–Pt + 10% Rh thermocouples, located near the external wall of the heater. It was found in the graduation experiment that the temperature difference between the sample and the heater was 15–20% of the difference between room temperature and the heater temperature; also the temperature difference between the centre of the sample and

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*Present address: Max-Planck Institut fur Chemie, Postfach 3060, D 6500 Mainz, Germany.

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the edges was 20% of the difference between the sample and room temperature.

Pressure changes at heating and phase transitions were fixed by the method of baro-thermal analysis (BTA) described elsewhere [13], in which the difference of thermo-electromotive force (thermo-e.m.f.) pressure dependences of the thermocouples was used. The volume change was evaluated from the BTA curve. The error in the pressure measurements was ±0.1 GPa at room temperature ±0.3 GPa after phase transitions accompanied by a change in the sample volume. Error was also increased at partial unloading of the sample, and at low initial pressures ($P < 0.5$ GPa) the hydrostatics was disturbed. The degree of hydrostatics is 0.25–0.35 GPa for lithograph stone [14] and 0.01 GPa for single-crystal NaCl [15].

Thus, using this technique, it is possible to melt the phosphorus with superheating without it escaping, to heat and quench the samples at different heating and cooling rates, and to control the volume changes of the sample during the experiments.

X-ray powder diffraction (XRD) was used for phase determination (X-ray camera $d = 114$ mm, $\lambda \mathrm{Cu}K_\alpha$). The density was defined using a long-necked pycnometer. A TECHNIVAL-2 microscope, equipped with a photocamera, was used for visual investigation and photographing the samples.

3. Results

Two marked peaks are observed on the BTA curves, on heating the red amorphous phosphorus, initially loaded to pressures $P = 0.6$–1.0 GPa (Fig. 1). The first peak corresponds to a decrease of pressure, which is connected with phase transition in black phosphorus. The second peak has the opposite volume effect, and is connected with melting of the black form. If we suppose that thermal and mechanical properties show no considerable changes on heating between the first and the second peaks, then the volume change at melting can be evaluated by a comparison of the areas under the BTA peaks.

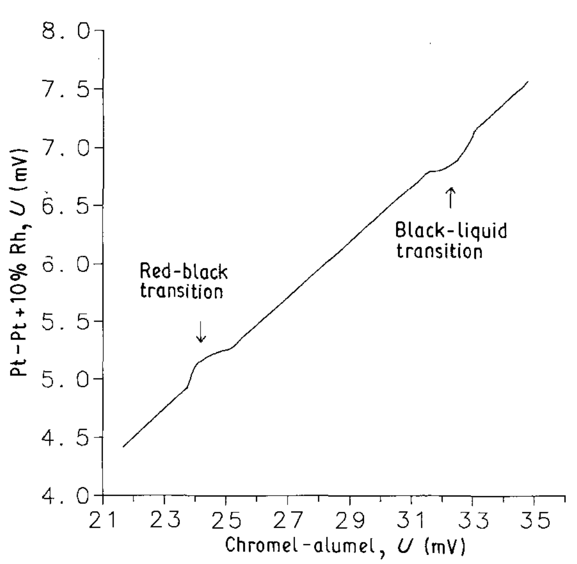

Figure 1 Thermo-e.m.f. of the Pt–Pt + 10% Rh thermocouple versus that of the chromel–alumel thermocouple in Experiment 1. Initial pressure $P = 0.5$ GPa, $T = 300$ K.

$\Delta V_{\mathrm{b}\to\mathrm{l}} \approx \Delta V_{\mathrm{r}\to\mathrm{b}}$, where $\Delta V_{\mathrm{b}\to\mathrm{l}}$ is volume change at black–liquid phosphorus transition and $\Delta V_{\mathrm{r}\to\mathrm{b}}$ is that at the red–black transition. When the initial pressure was $P = 0.3$–0.6 GPa, only one peak can be reliably registered at the heater temperature, $T_\mathrm{h} = 900$–1000 K ($\mathrm{d}T/\mathrm{d}t = 30\ \mathrm{K\,min^{-1}}$). At higher heater temperatures, $T_\mathrm{h} = 1050$–1250 K, there are some anomalies with opposite volume effects. Probably, they are connected with temperature gradients in a sample, where both processes take place simultaneously. The pressure diminishes when $\Delta P = 0.2$–0.4 GPa after the red–black phosphorus transition. On heating to $T_\mathrm{h} = 800$ K, the pressure increases no more than $\Delta P = 0.15$ GPa. If a sample is prepared from black phosphorus, then only one peak is observed on the BTA curves; this corresponds to the melting process.

A number of experiments was made to investigate relative stability of the red and black forms of phosphorus.

Experiment 1: Amorphous red (violet) phosphorus powder was the starting material ($\rho = 2.17 \pm 0.03\ \mathrm{g\,cm^{-3}}$), and the initial pressure was $P = 0.5 \pm 0.1$ GPa. The sample was heated to $T = 1000 \pm 50$ K ($T_\mathrm{h} = 1120 \pm 20$ K) at a heating rate of $\mathrm{d}T/\mathrm{d}t = 30\ \mathrm{K\,min^{-1}}$. The sample was held at these conditions for 2–3 min, and then slowly cooled at $-20\ \mathrm{K\,min^{-1}}$.

A compact sample, consisting of regions of red and black phosphorus was produced (Fig. 2; sample broken across the diameter). The density of the red pieces from this sample was $\rho = 2.33 \pm 0.08\ \mathrm{g\,cm^{-3}}$. XRD results are shown in Table 1; there is only a qualitative coincidence with the results of Frost.

Experiment 2: The same process was used as in the first experiment, except that the sample was cooled extremely quickly at $\mathrm{d}T/\mathrm{d}t = -10^4\ \mathrm{K\,min^{-1}}$ (rapid quenching). The sample consisted of black phosphorus with microscopic inclusions of the red form, being no more than 1% by volume (Fig. 3; sample again broken across the diameter). The measured density of the material was $\rho = 2.62 \pm 0.03\ \mathrm{g\,cm^{-3}}$. XRD results are presented in Table II. There is very

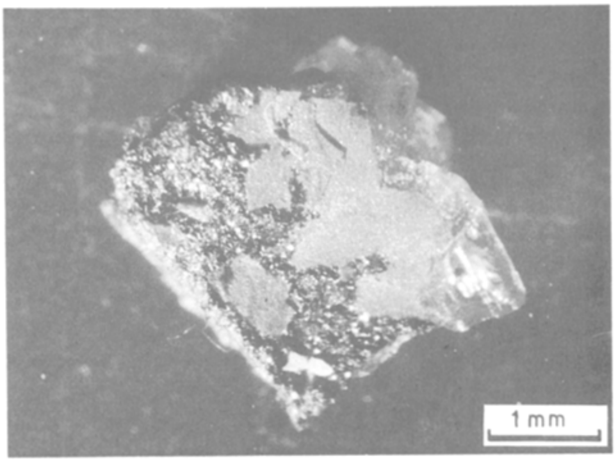

Figure 2 An example of the sample after processing as in Experiment 1. The smooth surface is red phosphorus and the granular surface is of black phosphorus.

TABLE I The red phosphorus; Experiment 1

d (nm)	I/I_0
0.581	Weak
0.544	Strong
0.514	Weak
0.337	Weak
0.304	Middle
0.289	Strong
0.282	Middle
0.271	Strong
0.262(5)	Strong
0.256	Middle
0.228	Middle
0.199	Middle
0.179	Middle
0.175	Middle
0.164	Weak
0.161(5)	Strong
0.157	Weak
0.145	Weak
0.142	Weak
0.140	Weak
0.129	Weak
0.126	Weak
0.120	Weak

TABLE II The black phosphorus; Experiment 2

d (nm)	I/I_0
0.512(5)	Middle
0.331	Middle
0.260	Strong
0.254	Strong
0.223(5)	Weak
0.217	Weak
0.210	Weak
0.200	Weak
0.179	Middle
0.174	Middle
0.167	Weak
0.165	Middle
0.163(5)	Strong
0.161	Strong
0.158	Weak
0.148	Middle
0.140	Strong
0.136	Weak
0.132	Weak
0.127	Weak
0.125	Weak
0.120	Middle
0.118	Weak
0.116	Middle

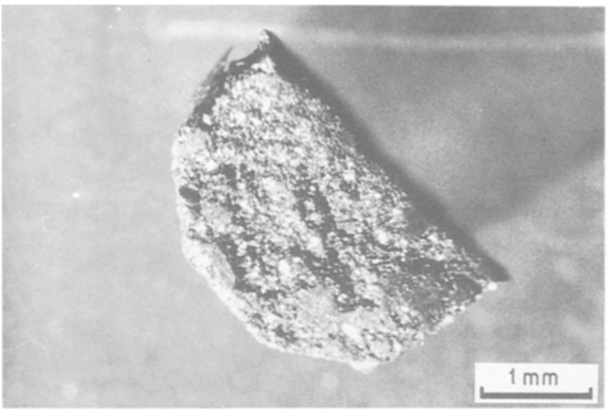

Figure 3 Example of sample after processing as in Experiment 2 and showing mainly black phosphorus.

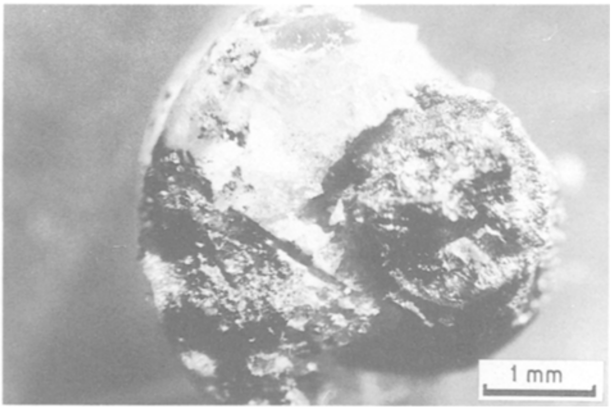

Figure 4 Example of sample after processing as in Experiment 3.

good agreement with the results Hultgren *et al.* [16], excluding two reflections which correspond to the interplane distances 0.167 and 0.165 nm.

Experiment 3: The starting material was black crystalline phosphorus, and the initial pressure was $P = 0.5 \pm 0.1$ GPa. The heating rate up to $T = 1050 \pm 50$ K ($T_h = 1150 \pm 20$ K) was $dT/dt = 30$ K min^{-1} and the melting of the sample was fixed by the BTA method. The pressure was then slowly decreased and the sample was cooled at $dT/dt = -10$ K min^{-1}. The resulting sample was dumb-bell shaped and contained mainly black phosphorus, with a thin layer of the red, 0.3–0.5 mm thick, on the periphery (Fig. 4; sample broken perpendicular to its axis). It was impossible to measure the density of the substance from this layer. XRD data of the substance scraped off the side of this sample are given in Table III. The reflections correspond to a mixture of black and red phosphorus.

Experiment 4: The procedure was the same as in Experiment 3, excluding the reduction in pressure in the liquid state. As a result a pure black phosphorus was obtained.

Experiment 5: Experiment 3 was repeated, but the pressure was released. In this case, phosphorus noticeably flowed out of the container, leaving in and around the container a mixture of red and white phosphorus. The white phosphorus immediately ignited on opening the container. Obviously, white phosphorus was generated after sublimation and subsequent precipitation of the sample, when a pressure of $P < 0.01$ GPa was reached.

4. Discussion

To date the red–black and black–liquid transitions have been investigated at pressures of more than 0.3 GPa [2, 10]. However, pressure region

TABLE III The mixture of red and black phosphorus; Experiment 3

d (nm)	I/I_0
0.575	Middle
0.521(5)	Middle
0.336	Weak
0.308	Weak
0.291	Weak
0.280(5)	Weak
0.262	Strong
0.256	Strong
0.226	Weak
0.211	Weak
0.199	Middle
0.179(5)	Weak
0.175	Weak
0.171	Weak
0.164	Middle
0.161(5)	Weak
0.141	Weak
0.126	Weak
0.116	Weak

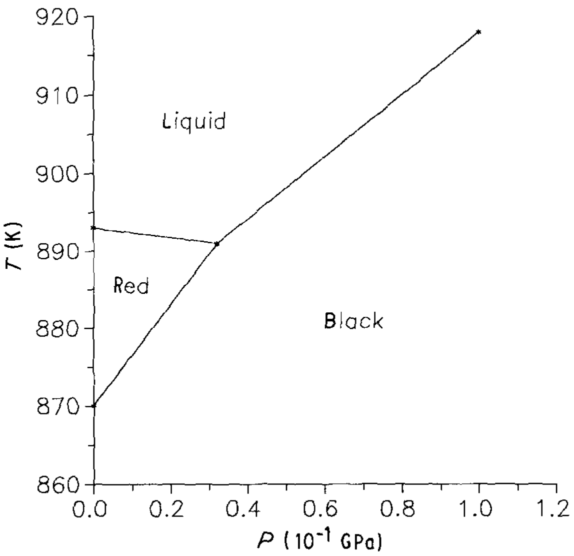

Figure 5 The possible P–T diagram of the stable region for red phosphorus, when $\Delta V_{b \to l} = 0.95 \Delta V_{r \to b}$.

0.01–0.3 GPa at high temperatures, remains *terra incognita* for phosphorus. The thermodynamical values for the various phosphorus forms show serious discrepancies [11, 17]. It is considered that red phosphorus has no region of stability on the P–T diagram. In this work, it was found that red phosphorus appears on crystallization of the liquid which was produced from black phosphorus at relatively low pressures, $P < 0.5$ GPa (Experiment 3). Crystallization of red phosphorus takes place in a region of maximal temperatures and slow cooling (Fig. 4). The results of Experiment 3 are supported by data from Experiments 1 and 2, where a pressure decrease induces the transition from red to black forms, on heating, accompanied by a considerable volume diminution of about 12%. Possibly, there is a region of red phosphorus stability near the liquidus.

Unfortunately, the experiments were only successful where the pressure was less than 0.5 GPa; because our equipment does not allow quantitative measurement of the pressure in this range with an accuracy better than ±0.2 GPa. Only a qualitative conclusion can be drawn about the possibility of the existence of red phosphorus on the P–T plane at pressures $P < 0.5$ GPa. The absence of flow and sublimation of the phosphorus in Experiments 1 and 3 indicates that the pressure was more than the critical value $P > 0.01$ GPa.

We attempted to evaluate the conditions of stability of the red, black and liquid states, using the enthalpy difference data for the red and black forms at room temperature [11] and at $T = 625$ K [17]; our results indicate a volume change at the melting point of black phosphorus from the BTA method, and give a value of the slope for black–liquid transition line [2]. A qualitative diagram is given in Fig. 5, in which the region of possible stability of the red phosphorus is presented. In our opinion, this diagram satisfies the experiment, if there is a reduction in the specific volume at melting point of red phosphorus. On the other hand, it is necessary to take into account the possibility of the simultaneous melting of black phosphorus and transition from the red to the black form due to the temperature gradient in the sample.

On slow cooling from the liquid state, crystallization of the stable (red) form at high-temperature and low-pressure ($P < 0.5$ GPa) occurs.

On comparing phosphorus with sulphur (its neighbour in Mendeleyev's Periodic system), sulphur is seen also to have a high-temperature monoclinic modification near the liquidus, which transforms to orthorhombic structure at high pressures or low temperatures. This supports our supposition, that the red form is the high-temperature modification of phosphorus. The red–black transformation line in [10] is, probably, a hysteresis line, which is connected to the extremely slow kinetics of this transformation.

5. Conclusion

The experimental results allow us to assume the existence of a region of red phosphorus stability at low pressures, but it is impossible to make quantitative measurements of the pressure using our equipment. It will be necessary to carry out a careful investigation in the pressure region $P = 0.01$–0.5 GPa, using hydrostatic equipment, for example, a gasostat, to determine this quantitatively.

Acknowledgements

The authors are grateful to Professor V. D. Blank and Professor S. V. Popova for attention to the work and useful discussions.

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Received 22 November 1990
and accepted 10 April 1991