Pis'ma v ZhETF, vol. 80, iss. 11, pp. 831 – 834

Amorphization of cuprite, Cu_2O, due to chemical decomposition under high pressure

V. V. Sinitsyn[1]*, V. P. Dmitriev*[+]*, I. K. Bdikin, D. Machon*[+]*, L. Dubrovinsky*[*]*, E. G. Ponyatovsky, H.-P. Weber*[△]

Institute of Solid State Physics RAS, 142432 Chernogolovka, Moscow District, Russia

[+] *Group "Structure of Materials under Extreme Conditions", Swiss-Norwegian Beam Lines at ESRF, F-38043 Grenoble, France*

[*] *Bayerisches Geoinstitut, Universitat Bayreuth, D-95440 Bayreuth, Germany*

[△] *LCr/IPMC/FSB, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland*

Submitted 3 November 2004

Using synchrotron radiation and a diamond-anvil cell, a structural study of the phase transformations in Cu_2O is carried out from diffraction data obtained in-situ while heating at a pressure of 30 GPa. Around 140 °C we observe a transition of Cu_2O to an amorphous state, with the amorphous state persisting to about 260 °C. Further heating up to 400 °C yields at first a nanocrystalline two-phase mixture of Cu+CuO; then with prolonged heating at 400 °C full crystallization of this mixture. The present structural data are the first experimental evidence of solid state amorphization under high pressure as an intermediate stage of the high-pressure decomposition of complex compounds.

PACS: 74.50.+r, 74.80.Fp

One of the topical fields in present high-pressure research is the study of amorphization occurring in initially crystalline substances. More than a hundred substances have been found to undergo solid-state amorphization (SSA) due to an appropriate thermobaric treatment [1, 2]. Normally, SSA is observed in substances with two polymorphous modifications of considerably different density in their equilibrium $T-P$-phase diagrams. The transition to the amorphous state takes place either in the phase of low-density upon compression or in the high-density phase upon decompression. Therefore, SSA is often considered as an intermediate stage of a "frozen" polymorphic transition. Several papers [2 – 4], however, have been reported where another SSA mechanism was proposed, namely that SSA resulted from slow decomposition of a chemically pure initial crystalline phase into two crystalline phases of other composition. Typical compounds where this effect is assumed include hydroxides such as $Ca(OH)_2$ and $Ni(OH)_2$ [2], rare earth molybdates [3] as well as many minerals that are Earth-core and mantle components and have complex chemical formulas [4]. In some substances the decomposition processes result in a considerable volume decrease which has led Meade and Jeanloz [5] to suggest that these processes might play an important role in triggering earthquakes. Unquestionably, a clarification of the physical processes of SSA and of mineral formation in the Earth interior is important. An experimental study of the transition sequence *pure crystalline compound* $\longrightarrow$ *amorphous state* $\longrightarrow$ *crystalline products of decomposition* **has so far not been carried out** *in situ*, and this study where we report on the first experimental observation of amorphization due to decomposition under pressure fills this gap.

To study the process experimentally, we chose cuprous oxide, Cu_2O. That Cu_2O decomposes under high pressure has been recognized previously [6]. The Cu_2O–Cu+CuO equilibrium line has been calculated, and the kinetic $T-P$-diagram was plotted experimentally, including the $Cu_2O \longrightarrow$ Cu+CuO decomposition line on compression and the reverse synthesis line, Cu+CuO $\longrightarrow Cu_2O$, on decompression [6]. The equilibrium pressure at 20 °C is $P = 4$ GPa, and the slope of the equilibrium line is $dT/dP = 250$ K/GPa. At $T = 350$ °C, Cu_2O decomposes around $P = 7$ GPa. At higher pressures the decomposition temperature decreases, but the slope of the decomposition line becomes less at $P > 8$ GPa so that the decomposition temperature is about 120 °C at the limit of the investigated pressure range, 10 GPa [6, 7]. Using thermobaric quenching experiments, it was found that Cu_2O under p, T conditions close to the decomposition line underwent a transition to the nanocrystalline state [7]. It is reasonable to assume therefore that all stages of decomposition, Cu_2O amorphization included, can be observed at higher pressures and lower temperatures when the diffusion of the decomposition products becomes slow.

[1] e-mail: sinitsyn@issp.ac.ru

The structural studies were performed at the Swiss-Norwegian beam lines (BM1A) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) by angle-dispersive diffraction techniques using monochromatic radiation ($\lambda = 0.7109$ Å). Diffraction patterns were collected with an image plate detector (MAR345). The sample-to-detector distance and the image plate inclination angles were precisely calibrated using a silicon standard. The two-dimensional diffraction images were analysed using the ESRF Fit2D software, yielding one-dimensional intensity vs. diffraction angle 2θ patterns [8].

In the experiment, pressure was increased to 30 GPa at room temperature in steps of about 10 GPa. The sample was maintained in each step for an hour in order to allow relaxation of the shear stress arising in the process of loading. Around 11 GPa, we observed a phase transition to a hexagonal phase II described earlier [9]. A further increase in pressure to 21 GPa resulted in a new diffraction pattern, indicative of a phase transition to a new crystalline modification, phase III. This phase remained on further pressure increase to 30 GPa, the maximum pressure applied. The analysis of the peak positions demonstrated that the reflections of phase III were well described within a simple hexagonal lattice with lattice parameters of $a = 5.86$ Å and $c = 18.78$ Å. This structure is rather different from the hexagonal $CdCl_2$-type reported earlier [9] in the same pressure range. We chose a different unit cell because additional reflections were observed. Taking these reflections into account, the a lattice parameter should be about doubled compared to the earlier data [9]. Note that the line of the $Cu_2O \Leftrightarrow Cu{+}CuO$ chemical equilibrium at room temperature is within the pressure range of 4 to 5 GPa; therefore the Cu_2O phase state is out of its stability range at $P > 5$ GPa. It is known that the features of the phase state formed in the region of its metastability may depend on the conditions of the thermobaric loading, that is, on hydrostaticity, on the initial grain size, on the compression rate, *etc.* Therefore, the difference in the structures observed here and in [9] can be due to different experimental conditions on compression.

At a pressure of 30 GPa, the sample was heated to 400 °C in steps of 20 to 40 °C, and diffraction patterns were measured at each step. Fig.1 shows representative diffraction patterns collected upon heating. Heating results in strong broadening of all phase III reflections, with two broad haloes observed at a temperature of about 140 °C (curve *2* in Fig.1). The haloes indicate sample amorphization; note that the maxima of the haloes lie at positions different than the positions of the strongest reflections of the hexagonal phase. It can therefore be assumed that the short-range order of the amorphous phase differs from that of phase III.

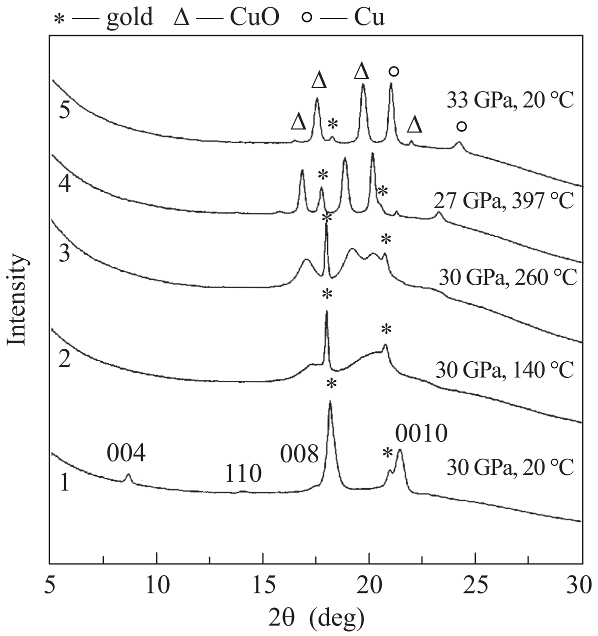

Fig.1. The diffraction patterns of Cu_2O at $P \approx 30$ GPa and different temperatures. The (hkl) indexes are shown for the high pressure hexagonal phase

Further increase in temperature leads to a gradual increase of the intensity of the first maximum while its width decreases. At temperatures of 240 to 260 °C and above, the second maximum splits into two broad peaks with nearly the same intensities (Fig.1, curve *3*). The emergence of peaks of lower intensity indicates onset of the recrystallization process. An estimation of the grain size from the half-width of the first maximum gives a value of about 6.5 nm, which is characteristic of the nanocrystalline state. The diffraction pattern demonstrates only quantitative changes in the temperature range of 240 to ~ 350 °C, that is, decreasing width of the sample reflections and their increase in intensity with respect to the lines of gold. The widths of the sample and gold reflections become comparable at $T = 400$ °C (Fig.1, curve *4*), evidence that the recrystallization process is complete. It is worth noting that the diameter of the gasket hole increases as temperature is increased, and, as a consequence, pressure in the cell somewhat decreases. To compensate this effect, we increased the load applied to the diamonds in the process of heating. This procedure, however, becomes rather complicated at high temperatures, therefore the 400 °C diffraction pattern was registered at a somewhat lower pressure value, $P = 27$ GPa.

The diffraction pattern remained the same upon cooling to room temperature followed by decompression, but for the shift of all X-ray lines. The X-ray analysis at atmospheric pressure demonstrated that the recrystallized mixture consisted of CuO and Cu. Both substances do not undergo phase transitions in the $T-P$-region of the study [10, 11] therefore the essentially invariable diffraction pattern on cooling and decompression is reasonable. Positions of the copper and copper oxide peaks after cooling the high-pressure cell are indicated in Fig.1 curve 5 (pressure increased to $P = 33$ GPa at the cooling run).

So, the following sequence of the phase transformations is observed in Cu_2O in the present experiment at a pressure of 30 GPa during heating:

$$\text{hexagonal phase} \xrightarrow{140\,^\circ\text{C}} \text{amorphous state} \xrightarrow{260\,^\circ\text{C}}$$
$$\xrightarrow{260\,^\circ\text{C}} \text{nanocrystalline state CuO+Cu} \xrightarrow{400\,^\circ\text{C}}$$
$$\xrightarrow{400\,^\circ\text{C}} \text{crystalline CuO+Cu mixture.}$$

The behavior of the diffraction spectrum at $T \geq 140\,^\circ$C suggests that both amorphous and, particularly, nanocrystalline states are formed as the products of the chemical decomposition reaction, $Cu_2O \longrightarrow CuO + Cu$. At low temperatures, Cu_2O decomposition is limited to a break of the chemical short-range order, resulting in amorphization. At $T \geq 240-260\,^\circ$C, nanocrystalline Cu and CuO nuclei begin growing. It is not unlikely that there is some temperature interval where one of the components recrystallizes and the other component stays amorphous, due to different diffusion mobilities of the components. This interval, however, appears to be narrow at 30 GPa because both components recrystallized simultaneously at the temperature variation steps of 20 to 40 °C.

Comparison of the present data and those from Refs. [6, 7, 9, 12, 13] results in the Cu_2O $T-P$-phase diagram outlined in Fig.2. The solid lines in Fig.2 represent the kinetic lines of the $Cu_2O \longrightarrow CuO + Cu$ decomposition and $CuO + Cu \longrightarrow Cu_2O$ synthesis, and the dashed line corresponds to the line of the $Cu_2O - CuO + Cu$ equilibrium calculated earlier [6, 7]. The equilibrium line divides the $P-T$-plane into two regions: the region of the thermodynamic stability of the Cu_2O compound is on left of the line, and the region of the CuO+Cu two-phase states is on the right. One structural phase transition, *cubic* (I)$-$*tetragonal* (Ia), concomitant with a small volume change, has been observed in the Cu_2O stability region [11]. The kinetic decomposition line is in the range between 120 and 150 °C at $P \geq 8$ GPa, therefore the Cu_2O compound can remain in the metastable state at room temperature well above the equilibrium pressure. In the Cu_2O metastable region, two phase transitions, Ia$-$II and II$-$III, take place at pressures of 10–12 GPa [7, 8] and ~18–21 GPa [8], respectively, they were also observed in the present experiment. The earlier decomposition curve has not been determined at pressures above 10 GPa, but our data show that the temperature for decomposition into crystalline states at pressures of 27–30 GPa is in the interval 390–400 °C. An increase of the decomposition temperature is therefore expected at $P \geq 10$ GPa, as shown tentatively with the dashed line in Fig.2. The region of the nanocrystalline states is in the close vicinity of the decomposition curve whereas the region of the amorphous states is extended to lower temperatures. The temperature intervals of these regions are rather narrow at pressure up to 10 GPa, which prevented the amorphous phase from being observed at pressures of 10–15 GPa in the previous works [7].

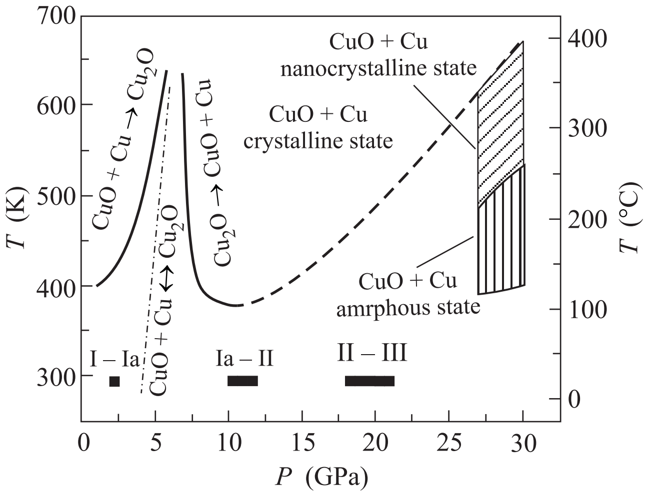

Fig.2. The $P-T$-phase diagram of Cu_2O in stable and metastable regions. The details are given in the text

This work was supported by the RFBR grant # 04-02-17143, by the RAS Program "Physics and mechanics of high compression substances and the internal problem arrangements of Earth and planets" and by the Research Cooperation Program grant SCOPE 2000 # 7SUPJ062362 of the Swiss National Science Foundation.

1. E. G. Ponyatovsky and O. I. Barkalov, Materials Science Reports **8**, 147 (1992).
2. S. M. Sharma and S. K. Sikka, Progr. Mater. Sci. **40**, 1 (1996).
3. E. G. Ponyatovsky, V. V. Sinitsyn, R. A. Dilanyan, and B. Redkin, Pis'ma ZhETF **61**, 217 (1995).
4. A. K. Arora, Solid State Comm. **115**, 665 (2000).
5. C. Meade and R. Jeanloz, Science **252**, 68 (1991).

6. I. T. Belash, G. I. Peresada, and E. G. Ponyatovsky, Neorganicheskie materiali (rus) **13**, 666 (1977).
7. E. G. Ponyatovsky, G. E. Abrosimova, A. S. Aronin et al., Phys. of the Solid State (Russian) **44**, 852 (2002).
8. A. P. Hammersley, S. O. Svensson, M. Hanfland et al., High Press. Res. **14**, 235 (1996).
9. A. Werner and H. D. Hochheimer Phys. Rev. **25**, 5929 (1982).
10. L. C. Bourne, P. Y. Yu. Zettl, and M. L. Cohen, Phys. Rev. **B40**, 10973 (1989).
11. E. Yu. Tonkov, High pressure phase transformations **1**, 328 (1992).
12. M. Kalliomaki, V. Meisalo, and A. Laisaar, Phys. Stat. Sol. **(a)56**, K127 (1979).
13. D. Machon, V. V. Sinitsyn, V. P. Dmitriev et al., J. Phys.: Condens. Matter, **15**, 7227 (2003).