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P-T phase diagram and structural transformations of molten P_2O_5 under pressure

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The P_2O_5 compound is an archetypical glass-forming oxide with a record high hygroscopicity, which makes its study extremely difficult. We present the *in situ* x-ray diffraction study of the pressure-temperature phase diagram of P_2O_5 and, particularly, of the liquid P_2O_5 structure under high pressure up to 10 GPa. Additionally, quenching from the melt has been used to extend the melting curve up to 15 GPa. We found that structural transformation in the liquid P_2O_5 under pressure is unique and includes three stages: first, the disappearance of the intermediate range order of the melt together with a slow increase in the average first-coordination number $\langle N_1 \rangle$ (P-O and O-P neighbors) up to 4 GPa; second, the "normal" compression almost without structural modification at higher pressures up to 8–9 GPa; and, finally, the abrupt change of the short-range order structure of the liquid with the jumplike $\langle N_1 \rangle$ increase at 9–10 GPa. The last stage correlates with the melting curve maximum (≈1250 °C) at ≈10 GPa and can be interpreted as a transformation to the liquid phase with entirely fivefold-coordinated phosphorus and twofold-coordinated oxygen atoms.

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Phase transformations in liquids under high pressure are one of the most intriguing and puzzling areas of physics [1]. Structural transformations in the oxide melts are responsible for atypical pressure dependences of their viscosities and glass-forming ability [2–4]. There is no experimental structural study of the most of oxide liquids under high pressure due to their very high melting temperature. The P_2O_5 substance ranks third among top network-forming oxides (after SiO_2 and B_2O_3) in terms of its use in glass products, and its melting temperature is relatively low. The P_2O_5 melt is a prototype of network-forming "strong" liquid; it has an extremely high viscosity and easily forms glass during cooling [5]. The notion of the P_2O_5 tetrahedra with three bridging oxygen atoms and one nonbridging terminal oxygen atom is commonly accepted for crystalline, vitreous, and liquid P_2O_5 substances (see, e.g., Ref. [6] and references therein). The compound is one of the most hygroscopic among all inorganic substances, and it is used in its pure form only as a dehumidifier. As a consequence, investigations of the structure and properties of pure P_2O_5 are rather scanty, even at normal pressure. Phosphorus pentoxide crystallizes in several polymorphs. The h-form that belongs to the hexagonal crystal family, being also a trigonal crystal system, is best known. It is a van der Waals molecular crystal, which consists of P_4O_{10} molecules. This is a metastable modification, and it transforms under heating to the more stable polymeric modifications (orthorhombic o-form and o′-form), which form networks of PO_4 tetrahedra connected via corner-sharing oxygen atoms. The relative stability and thermodynamics of different crystalline P_2O_5 polymorphs are summarized in Ref. [7]. The melting temperature of stable forms at low pressures is about 580 °C; the superheating about 50 °C above the melting temperature is possible because of a high viscosity of the corresponding melt [8].

Due to experimental difficulties, the structure of solid and liquid P_2O_5 under pressure, as well as the pressure-temperature (*P-T*) phase diagram of this substance, have not been studied at all. Moreover, to our knowledge, there was only one attempt to study the structure of P_2O_5 liquid even at low pressures [9]. There were several high-pressure studies of phosphate glasses, e.g., $(P_2O_5)_{0.73}(Y_2O_3)_{0.27}$ glass [10]. The theoretical study of P_2O_5 crystalline polymorphs under compression [11] shows that at very high pressures (20–25) GPa new modifications with penta- and hexa-coordinated phosphorus can appear. Recently, it has been found that quenching from the P_2O_5 melt under very high pressures make it possible to obtain densified glasses with the modified intermediate order structure [12]. The structural changes inherited by the glasses obviously have to be originated from the corresponding structural transformations in the P_2O_5 melt. This suggestion also stimulated an *in situ* structural study of the P_2O_5 melt.

This paper aimed at performing the experimental research of the *P-T* phase diagram of P_2O_5, with a special goal of studying the liquid P_2O_5 structure under pressure. This research involved *in situ* x-ray diffraction measurements up to 10 GPa and 1500 °C and quenching experiments from the melt at different pressures up to 15 GPa. The research performed has allowed us to elucidate the nature of the phase transformations in liquid P_2O_5 under pressure.

The *in situ* high-pressure–high-temperature structural study of the crystalline and liquid P_2O_5 were carried out by the energy-dispersive x-ray diffraction (EDXD) method in the SMAP180 press at the BL14B1 beamline of the SPring-8 synchrotron radiation facility. The EDXD technique is well established, having been used for decades; and it has been successfully applied previously for the quantitative structural study of many glasses and liquids under high pressure (see, e.g., Refs. [13–17]). The P_2O_5 powders (99.5% purity) were pressed into tablets in a dry argon box and placed in a container made of hexagonal BN or high-purity graphite. Removing the high-pressure cell from the inert atmosphere and placing it into the press did not take more than 20 s, which made it possible to avoid the sample hydration. For the structural study, the samples were 1.5−2 mm in diameter and 0.5–1 mm in height. A cubic press was used for generating high pressure

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up to 10 GPa in amorphous boron-epoxy cubes. Heating was produced by passing alternating current through a graphite heater. Temperature was measured with a chromel-alumel thermocouple. Pressure was determined from the equation of state of NaCl. A special assembly design with a set of heat protectors enabled us to maintain high temperatures (up to 1500 °C) for a long time—about 2 hours, which was necessary for taking the spectra. The structure of the melt has been studied at 11 different pressures in intervals from 0.5 to 10 GPa. The spectra were registered at different diffraction angles 2θ (from 3° to 18°), which made it possible to restore the liquid structural factor and corresponding radial distribution function (RDF) $4\pi r^2\rho(r)$ with sufficient accuracy. The RDF was calculated from the structural factor $S(Q)$ with the damping factor diminishing from 1 to 0 in the interval 9–10 Å^{-1} of the scattering wave vector. The liquid density under pressure was estimated using the corresponding data on the density of the crystalline o′- modification, taking into account the approximate values of the density jump at the melting curve.

In the quenching experiments with the subsequent *ex situ* study of samples, a toroid-type high-pressure device [18] was used for generating high pressures (1−15 GPa) and temperatures (800−1600 °C). The high-pressure assemblies were also mounted in the dry argon box. The cooling rates during quenching varied from 0.5 K/s up to 1000 K/s.

The pressure-temperature phase diagram of P_2O_5 is presented in Fig. 1. The irreversible h → o′ and glass → o′ phase transformations as well as the melting curve were detected by the *in situ* EDXD study up to 10 GPa. The temperature of both transformations slowly increases with pressure from ≈380 °C at low pressures to ≈600 °C at 10 GPa. There were no structural transformations to the high-pressure modifications with penta- and hexa-coordinated phosphorus atoms in this pressure range. The details of the structure and compressibility of the glassy phase, molecular h-phase, and polymeric o′-phase under pressure will be presented elsewhere. The melting temperature of the compound rapidly increases with pressure and reaches ≈1250 °C at 10 GPa. The *ex situ* study of the substance compressed to higher pressures suggests the existence of the melting curve maximum. At 15 GPa, the melting temperature is about 1100 °C. The quenching experiments allow us to estimate the viscosity of the melt [19]. The critical cooling rate necessary to obtain the glass rapidly increases with pressure from 1 K/s at 1 GPa reaching 1000 K/s at 10−15 GPa. The estimated viscosity in the vicinity of the melting curve varies within four orders of magnitude, from ∼5000 Pa·s at low pressures up to ∼0.5 Pa·s at 10 GPa.

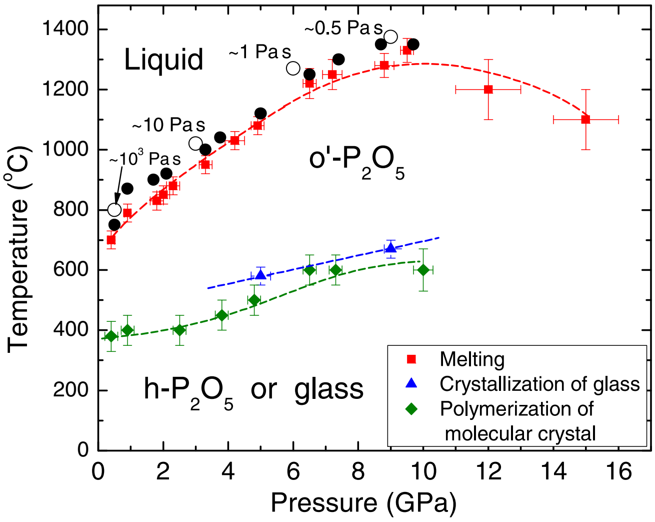

FIG. 1. (Color online) Experimental pressure-temperature phase diagram of P_2O_5, based on the EDXD measurements (up to 10 GPa) and quenching experiments (two melting points at $P > 10$ GPa). Solid circles correspond to points, where x-ray diffraction from the melt was recordered at different angles of the detector. Open circles are points of quenching experiments; the estimated viscosity values indicate the corresponding points. Dashed lines on the panel are guides for the eyes.

The results of the *in situ* EDXD study of liquid P_2O_5 are illustrated in Figs. 2 and 3. The total structure factor $S(Q)$ appreciably changes under compression. The intensity of the first diffraction sharp prepeak (FDSP) rapidly decreases with pressure [Fig. 2(a)], whereas its position shifts toward higher Q values [Fig. 2(c)] under compression up to ≈3.5 GPa. This prepeak corresponds to the intermediate range order in the melt [1]. At pressures higher than 3.5 GPa, the FDSP almost vanishes. The disappearance of an intermediate range order is a typical phenomenon for many organic and inorganic liquids. The Q position of the main first peak, determined by two different methods, decreases with pressure at the initial stage up to 3.5 GPa [Fig. 2(c)]. A further pressure increase leads to the "normal" compression behavior with the corresponding shift to higher Q values of the main peak position of $S(Q)$ up to 7−8 GPa. At higher pressures, this position "abnormally" decreases [Fig. 2(c)]. If we take into account the contribution of heat expansion, the positions of the FDSP and main peak of the melt perfectly match the corresponding positions for ordinary and densified glasses [12].

Analysis of the RDF of the P_2O_5 melt (Fig. 3), specifically of the first peak [Fig. 3(b)], details the pattern of structural transformations. Again, it is possible to recognize three intervals in the pressure dependencies of the first coordination sphere radius r_1 and the area under the first RDF peak N_1^{RDF} [Figs. 3(c) and 3(d)]. Normal homogenous contraction behavior corresponds to the very slow decrease of r_1 value and constant N_1 value. Below 4 GPa, both of the values slowly increase with pressure, which means a corresponding moderate increase in the P-O neighbors in the first coordination sphere. The further compression from 4 GPa to 8 GPa leads to simple contraction of the liquid (decrease of r_1) without a significant change in the coordination number. Finally, at the highest pressures, there is an additional abrupt increase of N_1, which can be clearly interpreted as an increase in the numbers of fivefold-coordinated phosphorus and twofold-coordinated oxygen atoms. Again, the values of N_1^{RDF} and r_1 in the melt at low pressures perfectly match [Figs. 3(c) and 3(d)] the corresponding values for ordinary and densified glasses [12], although the first peaks of RDF in the glasses are narrower [Fig. 3(b)].

For the binary system, $N_1^{\mathrm{RDF}} = 2 f_{\mathrm{P}} f_{\mathrm{O}} \langle N_1 \rangle \langle f \rangle^2$ [20], where $\langle N_1 \rangle$ is the first average coordination number ($\langle N_1 \rangle = (2/7) N_{\text{P-O}} + (5/7) N_{\text{O-P}}$), where f_{P} and f_{O} are the

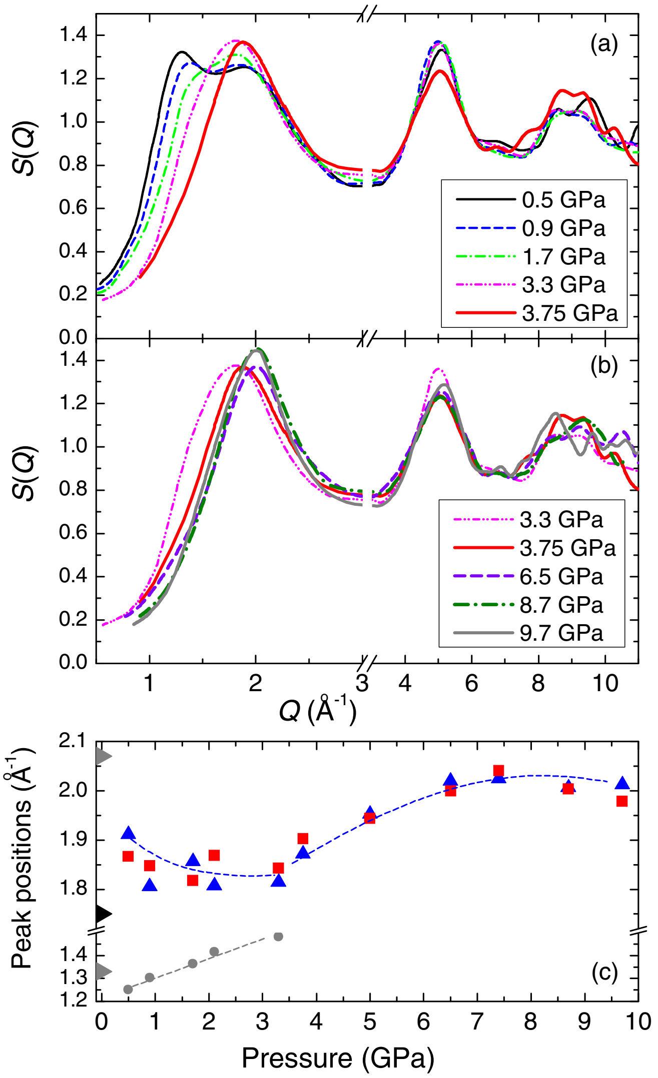

FIG. 2. (Color online) Calculated from the experimental EDXD data structure factors of the P_2O_5 melt at different pressures near the melting curve (a) and (b) together with Q positions of the prepeak (circles) and the first main peak (blue upper triangles are obtained from the peak maximum, and red squares—from the double or single gauss-peak fitting) of the structure factor $S(Q)$ (c). Right-side triangles correspond to ordinary (gray) and densified (black) glasses at normal conditions (from Ref. [12]). Dashed lines (c) are guides for the eyes.

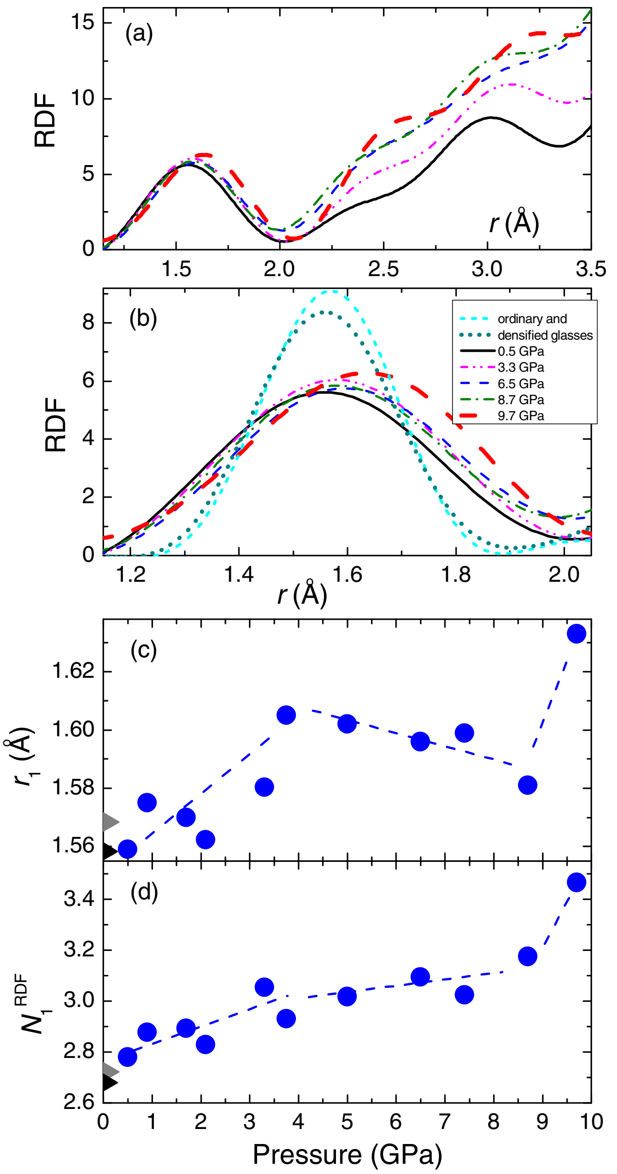

FIG. 3. (Color online) Radial distribution functions of the P_2O_5 melt at different pressures [(a) and (b) with the common legend] in comparison with those of P_2O_5 glasses at normal conditions from Ref. [12] (b) as well as the pressure dependences of the radius r_1 (c) and coordination number N_1^{RDF} (d) of the first-coordination sphere in the P_2O_5 melt, determined as the position of the maximum and the area under the radial distribution curve, respectively. (c), (d) Dashed lines are guides for the eyes, illustrating the basic trends of the pressure dependences.

corresponding atomic scattering factors and $\langle f \rangle = (2/7) f_B + (5/7) f_O$ for P_2O_5. In the first approximation, the f value is proportional to the full charge of the atom, i.e., $f_P \sim Z_P = 15$ and $f_O \sim Z_O = 8$. Thus, for molecular forms of P_2O_5, where each phosphorus atom has three twofold bridging oxygen neighbors and a single terminal oxygen neighbor (i.e., $N_{\text{P-O}} = 4$ and $\langle N_{\text{O-P}} \rangle = 1.6$), one can obtain $N_1^{\mathrm{RDF}} \approx 2.74$. This value is in excellent agreement with those for both the low pressure melt and glassy P_2O_5 at normal pressure [Fig. 3(d)]. On the other hand, for the P_2O_5 phase consisting of entirely fivefold-coordinated phosphorus and twofold-coordinated oxygen atoms ($N_{\text{P-O}} = 5$ and $N_{\text{O-P}} = 2$), $N_1^{\mathrm{RDF}} \approx 3.43$, which is quite close to the N_1^{RDF} value for the P_2O_5 melt at 10 GPa. At the intermediate stage between 4 and 9 GPa, $N_1^{\mathrm{RDF}} \approx 3$, which implies 40–50% of P being fivefold-coordinated by oxygen. The r_1 increase at the first ($P < 4$ GPa) and third ($P \approx 9$–10 GPa) stages of transformations in the melt [Fig. 3(c)] completely corresponds to the pattern drawn above, since terminal oxygen neighbors are at a shorter distance with respect to the central phosphorus atom then the bridging ones.

The disappearance of an intermediate range order at the beginning of compression corresponds to the closure of nanovoids, and the structure of liquid P_2O_5 at $P \geq 4$ GPa is similar in this respect to the structure of the densified

P_2O_5 glass [12]. The irreversible densification at 4–5 GPa was observed previously in phosphate-based glasses [10]. On the other hand, there is a significant change in the first coordination number in the liquid at this pressure, whereas phosphorus atoms in the densified glass remain fourfold-coordinated by oxygen. Obviously, under compression at quite high temperatures, there is a high probability for an "opening" of double bonding for terminal oxygen atoms and the formation of fivefold-coordinated phosphorus atoms. After cooling and decompression, these states should become unstable. At pressures higher than 8 GPa, PO_4 tetrahedra approach each other very closely and become extremely distorted. The avalanche additional opening of double bonding for the rest of terminal oxygen atoms and the abrupt coordination increase in the first sphere leads to the first-order-like transition in this pressure range.

The structural transformation in the liquid P_2O_5 results in a rapid increase of the melt density. It flattens the melting curve at pressures higher than 7–8 GPa and leads to the maximum on the melting curve at pressures around 10–11 GPa (Fig. 1). Phase transitions in the crystalline P_2O_5 with the formation of penta- and hexa-coordinated phosphorus atoms can occur at higher pressures about 20 GPa [11]. Thus, the P_2O_5 melt is possibly denser than the corresponding crystal in the 12–20 GPa pressure interval. A rapid decrease in the melt viscosity with pressure along the melting curve is obviously associated with the corresponding structural changes. The appearance of the "over-coordinated" PO_5 and PO_6 units is responsible for the acceleration of the diffusion of the atoms in the P_2O_5 covalent network-based liquid similarly to the high-pressure behavior of B_2O_3 liquid, where BO_4 units are responsible for the viscosity decrease [4].

In summary, we presented the results of the first direct *in situ* x-ray diffraction study of P_2O_5 liquid under high pressure. This oxide melt demonstrates quite an unusual structural behavior under compression. The anomalous behavior is associated with the unique structure of the P_2O_5 substance containing the double-bonded terminal oxygen atoms. The coordination in P_2O_5 liquid under high pressure changes from four to five for phosphorus atoms in two steps: The first step corresponds to a smooth structural transformation, whereas the second one corresponds to a sharp phase transition. The transformations in P_2O_5 melt result in the maximum on the melting curve and the rapid decrease of the liquid viscosity along the melting curve. The study at higher pressures is necessary for finding transitions in both the liquid and solid P_2O_5 to the predicted modifications with hexa-coordinated phosphorus atoms.

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