High-pressure phase diagram of O₂ and N₂ binary system: formation of kagome-lattice of O₂

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Abstract. High-pressure phase diagram of O₂ and N₂ binary system has been investigated using an x-ray diffraction method and the pressure-composition phase relation has been proposed up to 12 GPa. From the result, a hexagonal alloy phase reported previously was stable in relatively wide pressure and composition ranges. The structure of this phase was also determined to be a hexagonal lattice (space group: P6/mmm) with seven molecules in the unit cell from the Rietveld refinement. In this phase, formation of a new magnetic lattice of O₂: the kagome-lattice has also been proposed.

1. Introduction
Oxygen molecule is a micro-magnet with the magnetic moment of 2μ₀ perpendicular to the molecular axis. In the P-T phase diagram of oxygen, a rich polymorphism appears to reflect the magnetic interaction between oxygen molecules [1-7]. Recently, for the oxygen and nitrogen binary system, it has been also reported that the variety of solid phases occur in the pressure-composition phase diagram at room temperature [8,9]. In particular, appearance of a new alloy phase, which does not occur for either pure component, has been proposed [9]. Though the phase has been assigned to a hexagonal lattice [9], the detail of the structure still remains unknown. Though the phase boundaries of the new phase have also been investigated by the Raman scattering method [8] or a visual observation with a microscope [9], there is no detailed study on the phase transition from the structural aspect.

Our interest is focused on the hexagonal phase because the new magnetic order state of the oxygen molecule is expected in this phase. In this paper, the crystal structure of the new phase and the high-pressure phase diagram of the binary system at room temperature have been investigated by examining x-ray diffraction patterns.

2. Experimental
Mixtures of oxygen and nitrogen gases were used as a sample. The O₂ concentrations of the mixture samples measured in this study were 38, 43, 48, 60, 70 and 85 mol%. The concentration was measured by a magnetic oxygen meter and its error was within ±0.5%. A diamond anvil cell (DAC) was used as a high-pressure vessel. The mixture gases were liquefied at 77 K then confined into a DAC in a
cryostat. Pressure was determined by a ruby fluorescence method. For determination of the crystal structure of the new alloy phase, it was indispensable to obtain a fine powder sample. In this study, the powder sample was prepared by mean that the mixed liquid of 48%O₂ was rapidly compressed at low temperature of 77 K and annealed at ambient temperature. Powder x-ray diffraction experiments were carried out at 298 K using angle dispersive method with a monochromatic x-ray of 25 keV or 30 keV on the BL10XU beamline at the SPring-8 [10]. Powder patterns were collected in the pressure increasing cycle. Then the sample was oscillated by ±5° during x-ray exposure. Raman scattering measurements [11] were additionally carried out to confirm phase transitions.

3. Results and Discussion
First, the 48%O₂ sample was studied by the x-ray diffraction method. In the run, phase transitions from fluid to the cubic (Pm3n: δ-N₂ type [12] or γ-O₂ type structure) phase and next to the hexagonal phase were observed at 4.6 GPa and 8.2 GPa, respectively. And further at 11 GPa, the hexagonal phase caused the phase separation in the pure monoclinic ε-O₂ and cubic δ-N₂. The representative 2θ-intensity patterns of these phases are shown in figure 1. The pattern of the hexagonal phase at 9.5 GPa was well explained with the lattice constants of a = 5.6016(4) Å, c = 6.1645(8) Å and V = 167.52(6) Å³. The parameter c was one half of that proposed previously [9].

![Figure 1](image1.png)

**Figure 1.** The representative 2θ-intensity patterns of high-pressure phases for the 48%O₂ sample. Hollow patterns come from the fluid were observed Below 4.6 GPa. At 4.6 GPa, the sample solidified and the diffraction images composed of spotty Bragg reflections. The pattern of the cubic phase at 7.9 GPa was well indexed with the lattice constant of a = 5.873(1) Å and the hexagonal phase at 9.5 GPa was done with a = 5.6016(4) Å, c = 6.1645(8) Å. The pattern at 14.6 GPa, which was collected after annealing at 473K, was explained as a mixture of the pure ε-O₂ and δ-N₂ phases from molecular volumes shown in figure 2.

![Figure 2](image2.png)

**Figure 2.** The pressure dependence of the average volume per one molecule for the 48%O₂ sample obtained from the x-ray diffraction experiments, together with those of the pure O₂ (broken line) [4] and N₂ (dotted line) [13]. The present experimental data are shown by circles. The values, after the phase separation shown by diamonds, were estimated from the experimental data considering the composition. From the result, the number of molecules in the unit cell Z for the hexagonal phase was determined to be 7.
Figure 2 shows the pressure dependence of the average volume of one molecule for the 48%O₂ sample obtained from the x-ray diffraction experiments. Data for pure oxygen and nitrogen are also plotted for comparison. The values after phase separation were estimated from the present experimental data on the basis of the composition. From the result, the number of molecules in the unit cell Z for the hexagonal phase was determined to be 7 considering the volume-pressure relationship.

Figure 3 shows the diffraction pattern and image of the new hexagonal phase of 48%O₂ sample at 9.0 GPa, which was prepared by means of rapid compression at low temperature. The diffraction image consists of Debye rings but the size of the crystal grain seems slightly larger. The pattern was well indexed as a hexagonal lattice with the lattice constants of a = 5.644(1) Å, c = 6.172(1) Å, V = 170.28(6) Å³. It is found from figure 2 that the condition of Z = 7 satisfies the volume-pressure relationship. By the Rietveld simulation [14], the space group of the hexagonal lattice was finally determined to be P6/mmm (191) from candidates of 16 space groups. In this analysis, all molecules were assumed to be oxygen molecules with the atomic distance of 1.204 Å because it was difficult to distinguish nitrogen and oxygen with similar atomic scattering factor. As the result, the pattern was largely explained by a structural model with 3 molecules in the 6(i) site, 2 molecules in the 2(e) site and 2 molecules in the 4(h) site. In addition, the rotational disorder of molecules was simulated by placing 1/8 or 1/12 atoms into 24(r) site for each molecule. A structure model with freely rotating molecules placed in the 2(e) and 4(h) sites and almost rigid diatomic oxygen molecules centred at the 6(i) site reproduced good fit in the observed diffraction pattern with the reliability factors Rwp and R1 of 8.7% and 3.8%, respectively. Positional parameters of atoms are summarised in table 1. Atoms labelled by O1 & O2, O3 & O4, and O5 & O6 occupy the 6(i), 2(e), and 4(h) sites, respectively.

**Figure 3.** The diffraction pattern and image of the hexagonal phase of the 48%O₂ sample at 9.0 GPa. The diffraction image consists of Debye rings but the size of the crystal grain seems slightly larger. By a Rietveld analysis, the pattern was well explained as a structure model of S.G.: P6/mmm with 3 molecules in the 6(i) site, 2 molecules in the 2(e) site and 2 molecules in the 4(h) site.
Table 1. Structure parameters of the hexagonal phase at 9.0 GPa and 298 K.

| atom | site | $x$     | $y$     | $z$         | occupancy | number |
|------|------|---------|---------|-------------|-----------|--------|
| O1   | 24r  | 0.45126 | 0.01451 | 0.08505     | 1/8       | 3      |
| O2   | 24r  | 0.48778 | -0.04451| -0.09437    | 1/8       | 3      |
| O3   | 24r  | 0.12134 | 0.05743 | 0.30676     | 1/12      | 2      |
| O4   | 24r  | -0.0644 | 0.05585 | 0.20972     | 1/12      | 2      |
| O5   | 24r  | 0.48152 | 0.18826 | 0.41457     | 1/12      | 2      |
| O6   | 24r  | 0.70324 | 0.34142 | 0.49005     | 1/12      | 2      |

Figure 4. The structure model of the hexagonal (P6/mmm) phase. The rotational disorder of molecules was simulated by placing 1/8 or 1/12 atoms into 24(r) sites for each molecule. The molecules in the 6(i) site form a kagome lattice and their molecular axes are almost parallel to the c axis due to the orientational order while molecules in the other sites are freely rotating.

Figure 5. The phase relation of the O$_2$ and N$_2$ binary system in the range between 38 and 100% O$_2$ concentration. The symbols of semicircles represent the coexistence of two phases. It is found that the hexagonal phase (P6/mmm) is stable in the wider pressure and composition ranges than the previous report [9].

The structure model is illustrated in figure 4. The molecules in the 6(i) site form a kagome lattice and their molecular axes are almost parallel to the c axis due to the orientational order while molecules in the other sites are freely rotating. The nearest neighbour distance of molecules on the kagome lattice is 2.823 Å and comparable to that of the triangle-lattice 2.83 Å in the β phase of the pure O$_2$ at 6 GPa.
The distance for molecules in the other sites is more than 3 Å. The radii of major and minor axes of the ellipsoidal N$_2$ are 4% and 7% larger than those of O$_2$, respectively. Considering the molecular geometry, it is plausible that oxygen molecules occupy the 6(i) site while nitrogen molecules do the 2(e) or 4(h) site. In fact, the hexagonal phase occurs at the O$_2$ concentration of 43% or more (figure 5), filling fully the 6(i) site with oxygen molecules. Excess oxygen molecules would occupy the 2(e) or 4(h) site substitutionally. Therefore, the hexagonal phase may be stabilized by the magnetic interaction among oxygen molecules on the kagome lattice. It is interesting that oxygen molecules with a spin quantum number S = 1 per molecule form the kagome lattice of a geometrically frustrated magnetic system. This proposition can be demonstrated by the neutron diffraction measurement, which enables to identify whether the 6(i) site is fully occupied by oxygen molecules. Magnetic measurement is our challenge for the future.

Phase relation of the six samples with O$_2$ compositions of 38, 43, 48, 60, 70 and 85 mol% obtained by x-ray diffraction experiments was summarized in figure 5. From the present result, it is found that the hexagonal phase is stable in the wider pressure and composition ranges than previous report [9]. In the region of higher O$_2$ concentration, the pure β-O$_2$ phase (R-3m) precipitated from the hexagonal phase or the cubic phase with increasing pressure and coexisted with these phases. At the O$_2$ compositions of 38 and 43 mol%, the hexagonal phase was coexisted with the cubic phase. At higher pressures than around 10 GPa, the phase separation was observed in the hexagonal phase. Since the precipitation and separation of the phase are accompanied with the long-range diffusion of molecules in the solid phase, the phase boundary would depend on the interval of time for the x-ray measurements and include a certain level of uncertainty.

Figure 6 shows pressure change of Raman shift of vibron for oxygen and nitrogen molecules of the 48%O$_2$ sample. Raman spectra exhibited clear changes in response to phase transitions. In the cubic phase with two different sites in the unit cell, vibron band splits into two. At the transition to the hexagonal phase, two vibron bands become singlet. As the hexagonal phase has three molecular sites, oxygen and nitrogen molecules selectively occupy these sites, that is, oxygen molecules would do the 6(i) site. The behaviour of the spectra is in good agreement with previous report [8]. The pressures of the fluid-cubic and cubic-hexagonal transition well correspond to the results of the x-ray diffraction experiments. The cubic-hexagonal phase transition occurred rapidly and no remarkable hysteresis was observed at the transition in the pressure increasing and decreasing cycle.

**Figure 6.** The pressure evolution of Raman shift of vibrons for oxygen (a) and nitrogen (b) molecules of the 48%O$_2$ sample at room temperature.
On the other hand, during the phase separation at 10-12 GPa, two extra vibron bands of oxygen were observed with weak intensity. The bands may come from O$_2$ included in δ-N$_2$.

4. Conclusion
The hexagonal alloy phase was stable in a relatively wide pressure and composition range and the structure was assigned to space group: P6/mmm of $Z = 7$. In this phase, it was proposed that oxygen molecules form the kagome lattice of a geometrically frustrated magnetic system.

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