Structural and Optical Studies on Metallization of Oxygen

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Powder x-ray diffraction and infrared absorption experiments of solid oxygen at room temperature have been carried out up to 151 GPa and 60 GPa, respectively. The structural transition from the $\epsilon$ to $\zeta$ phase observed at 96 GPa in our previous experiment was reproduced. Stability of the $\zeta$ phase was confirmed up to 151 GPa. In infrared absorption experiments with a single-crystal of the $\epsilon$ phase, the IR-active vibron fundamental around 1500 cm$^{-1}$ split into at least three bands. The pressure dependence of frequency of the IR vibron fundamentals had a minimum at 20 GPa and above 30 GPa showed positive pressure coefficients between 1.2-1.7 cm$^{-1}$/GPa.

1. Introduction

Pressure-induced metallization and molecular dissociation of solid oxygen with molecular magnetism have attracted special interest with a view to understanding the fundamental effect of chemical bonding and novel electronic and magnetic properties of the resultant high-pressure phases. Recently, our high-pressure x-ray diffraction studies on solid oxygen, O$_2$, have revealed a structural transition from the $\epsilon$ phase at 96 GPa[1]. Since the transition corresponds to metallization reported by Desgreniers et al.[2], the high-pressure phase, $\zeta$, has been considered to be a (semi)metal. High-pressure Raman scattering study has reported dumping of the Raman-active vibron band in the intensity with pressure and the band became undetectable at the transition. The result supports that the $\zeta$ phase is metallic. However, these experimental results do not provide any positive evidence of molecular dissociation of O$_2$ molecules.

As for the $\epsilon$ phase, the single crystal analysis by Johnson et al.[4] have proposed the space group of C2/m. Previous infrared (IR) absorption study[5] to 20 GPa has reported observation of one IR-active vibron fundamental and its negative pressure dependence. But the atomic positional parameters and molecular site of O$_2$ in the monoclinic cell have not been determined. In order to research molecular dissociation of O$_2$ and the molecular vibration, powder x-ray diffraction experiments and IR absorption experiments were carried out up to a higher pressure than the previous studies[1,5].

2. Experimental

Liquid oxygen was loaded into a hole of a metal gasket in a DAC at a low temperature of 77 K and used for the sample. Powder x-ray diffraction experiments of solid oxygen of a light element were performed by using synchrotron radiation sources of $\lambda=0.4249$ Å in the ESRF and $\lambda=0.4988$ Å in the PF. Powder patterns were obtained by the angle dispersive method with a DAC and an image-plate detector[1]. IR absorption spectra at room temperature were taken by using a JASCO MFT-2000, micro-optical Fourier-transform spectrometer with a cooled Hg-Cd-Te detector. In the present work, we could detect splitting of absorption due to the IR fundamental by using a single crystal sample of the $\epsilon$ phase. Powder samples of the $\epsilon$ phase gave a strong absorption due to the IR-active vibron fundamentals. Absorbance was over 2 and the peak intensity saturated. The single crystal was prepared by the strain anneal method under high-pressure and high-temperature conditions of about 25 GPa and 650 K in a Merrill-Bassett type DAC with type Ila diamonds. The crystals exhibited a remarkable dichromatic character. Pressure was determined by a ruby fluorescence method[6] and the equation of state of Re[7].

3. Results and Discussion

Figure 1 shows a typical diffraction pattern of the $\epsilon$ phase. The pattern is well assigned to the base-centered monoclinic lattice proposed previously[4]. Calculated lattice constants are $a=7.827$ Å, $b=5.526$ Å, $c=3.678$ Å, $\beta=116.1^\circ$, and $Z=8$. The values agree with our previous result[1]. The powder pattern is similar to that by Desgreniers and Brister[8] except for the difference in the relative intensity of (001) reflection at $2\theta=7.5^\circ$ and (002) at $2\theta=15^\circ$. The difference results from the preferred orientation of the powder crystals in the sample chamber.

Figure 2 shows the pressure change of the powder pattern of solid oxygen up to 151 GPa at room temperature. Symbols G represent the peaks from a Re gasket. In the pattern at 66 GPa eight diffraction peaks are observed and well assigned to the monoclinic lattice of the $\epsilon$ phase. With increasing pressure, the diffraction pattern at 114 GPa shows an obvious change around 2$\theta=14^\circ$. The change is ascribed to the structural transition from the $\epsilon$ to $\zeta$ phase observed previously[1]. In this pattern of the
Fig. 2. Pressure change of the powder pattern of solid oxygen to 151 GPa. Symbols G represent the peaks from a Re gasket.

The ζ phase, only four diffraction peaks are observed due to broadening of the diffraction peaks and overlapping with a gasket peak though six diffraction peaks were observed previously[1]. With increasing pressure, the patterns of the ζ phase do not represent any sign of structural transition up to 151 GPa.

Figure 3 shows the pressure dependence of the d-values of the diffraction peaks together with previous data[1]. Open and solid circles represent the present and previous data, respectively. The present data are in good agreement with the previous data. We can clearly see that the structural transition occurs at 96 GPa. In this study, the structural transition from the ε to ζ phase was reconfirmed and the stability of the ζ phase was also confirmed up to 151 GPa.

Figure 4 shows a typical IR absorption spectrum of the ε phase. A frequency region between 1800 and 2400 cm⁻¹ obscured by absorption due to the diamonds is excluded. Strong absorption is observed around 1500 cm⁻¹. The absorption comes from the IR-active vibron fundamental and was shown to consist of at least three absorption bands from Lorentzian-curve fitting. These absorption bands showed a remarkable polarization property and two band with lower frequency vanished with the incident light properly polarized to the single-crystal sample. Agnew et al.[5] have reported from the experiment by using a mixed isotope sample of ¹⁶O₂ and ¹⁸O₂ that the IR vibron fundamental absorption of diamonds.
mental was a singlet. The present results claim that the IR vibron fundamental is at least a triplet in the pressure range of our experiment. Doubling of the Raman band is not observed. The mutual exclusion of IR and Raman vibron suggests that the structure of the $\varepsilon$ phase is centric. The observation of one Raman and three IR vibrons also suggests that the primitive cell must contained at least four $O_2$ molecules.

Figure 5 shows the pressure dependence of frequency of three IR vibron fundamental together with the Raman-active vibron. The data of the powder sample are also illustrated by broken lines. The broken line shows a saturating region of absorption due to the IR vibron fundamentals. With increasing pressure, the frequency of IR vibron initially decreases and then turns over with a minimum around 20 GPa. The pressure dependence of the highest frequency band agrees with previous result[5]. The pressure coefficients of three IR vibron estimated above 30 GPa are between 1.2 and 1.7 cm$^{-1}$/GPa. Raman vibron also shows a similar turn-over at 13 GPa. Estimated pressure coefficient was 2.3 cm$^{-1}$/GPa and larger than those of IR vibrons. Agnew et al. have pointed out the weakening of O-O bond from the behavior of Raman and IR vibron in the lower pressure region than 20 GPa. Observation of the turn-over suggests that the weakening is not always exact above 25 GPa.

The spectrum in Fig.4 also shows six combinations around 3000 cm$^{-1}$ and two combinations around 4400 cm$^{-1}$. The large number of combination bands may suggest that IR vibron fundamental is not singlet. Figure 6 shows the pressure dependence of the combination bands around 3000 cm$^{-1}$. The dependence of three bands with higher frequency, which slightly differ from that of three bands with lower frequency, can be assigned to combinations between Raman and IR vibron fundamentals. Three bands with lower frequency may be explained to combinations among three IR fundamentals considering the exclusion of the second overtone in the centric lattice.

The proposed centric lattice of $C_2/m$ contained four $O_2$ molecules in a primitive cell. The site symmetries are $C_1(4), C_5(2), 2C_2(2), 4C_4(1)$. The correlation method provided three site symmetries with IR-active vibron, $C_1, C_5, C_2$. The $C_1, C_5$, and $C_2$ molecular sites allow two Raman-active vibron and two IR-active vibron, one Raman and one IR, and one Raman and one IR, respectively. Therefore, three IR-active vibrons could not be explained even if four $O_2$ molecules center on any symmetry sites. Definite vibrational mode assignments of the $O_2$ stretching in the $\varepsilon$ phase can be made when the atomic positins are known. Further detail structural analysis of the single-crystal of the $\varepsilon$ phase by using the synchrotron radiation source is needed.

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References