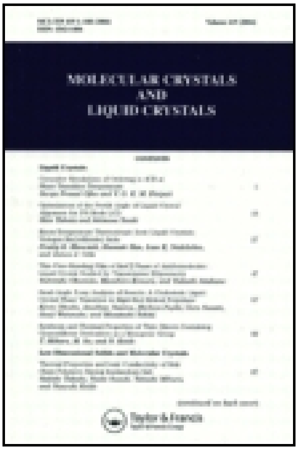

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Shear Stress Effect on the Absorption Spectra of Organic Thin Films Under High Pressure

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Shear Stress Effect on the Absorption Spectra of Organic Thin Films Under High Pressure

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The effects of shear stress on the absorption spectra of a thin film of one-dimensional bis(diphenylglyoximato)platinum(II), Pt(dpg)$_2$ have been studied under high pressure. The color of the thin film turns from red-brown at ambient pressure to green at 0.4 GPa. Then, one sapphire anvil is rotated by applied force in order to generate shear stress at 0.4 GPa. The color of the thin film at the outer part on the anvil changes remarkably from green to yellow, but the color at the center is green. The absorption spectra of Pt(dpg)$_2$ have simultaneously been measured under shear deformation and non-hydrostatic conditions. The absorption intensity of the visible band decreases sharply at outer part, and this absorption peak abruptly shifts to the near-infrared region. The powder x-ray diffraction profiles of the thin film of Pt(dpg)$_2$ at center and outer parts have been studied under shear deformation. The 110 and 200 lines at outer part markedly shift to the lower d-value region. In contrast, both diffraction lines at the center part are insensitive to shear stress. This behavior corresponds to the shift of the absorption band at outer part.

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Keywords: absorption spectrum; high-pressure; shear stress; thin film; x-ray diffraction

INTRODUCTION

Absorption bands of one-dimensional bis(diphenylglyoximato) platinum(II), $Pt(dpg)_2$ are rapidly shift to longer wavelength region with increasing pressure [1]. Then, the color of $Pt(dpg)_2$ remarkably turns from red-brown at ambient pressure through brown, green to greenish yellow and yellow up to 2 GPa. The structure of the complex is orthorhombic, space group Ibam [2]. The complex crystallizes in the columnar structure with linear metal chains. Powder x-ray diffraction of $Pt(dpg)_2$ has been studied with synchrotron radiation at high pressures. $Pt(dpg)_2$ is the most compressible compound [3].

We have prepared a new sapphire-anvil cell to generate shear stress at high pressure [4]. After two anvils are pressurized, the shear stress is generated by the rotation of one anvil at high pressure. Using the sapphire-anvil cell, the shear stress effects on the absorption spectra of $Pt(dpg)_2$ have been studied under high pressure. Further, a new shear-deformation diamond-anvil cell (SDAC) is designed in order to study x-ray diffraction under shear deformation and non-hydrostatic conditions. The x-ray diffraction patterns of $Pt(dpg)_2$ have been studied with the SDAC. We have *in situ* observed the shear stress effects on the absorption spectra and x-ray diffraction patterns of the thin films of $Pt(dpg)_2$ under high pressure.

EXPERIMENTAL

Using the sapphire-anvil cell, the absorption spectra of the flat film on the anvil were measured at several points along the radial direction under shear deformation and non-hydrostatic conditions. The thin film of $Pt(dpg)_2$ was prepared by evaporation onto the sapphire-anvil in a vacuum of ca. 10^{-6} Torr. The thickness of the thin film was about 1500 Å. The new diamond-anvil cell (SDAC) designed to generate shear stress was prepared. By use of synchrotron radiation, x-ray diffraction of the thin film of $Pt(dpg)_2$ was measured with the SDAC under shear deformation and non-hydrostatic conditions. The synchrotron radiation experiments were performed at the BL04B2 in the SPring-8 with the approval of Japan Synchrotron Radiation Research Institute (Proposal No.0280 2004A). The x-ray beam of $\lambda = 0.4966$ Å was collimated to 40 nm in diameter. The x-ray diffraction patterns of the flat film on the anvil were measured as a function of the position (r) along the radial direction under shear deformation.

RESULTS AND DISCUSSION

Absorption bands of the thin film of $Pt(dpg)_2$ are observed at around 380 and 550 nm at ambient pressure. The 380 nm band is ascribed to the metal to ligand charge-transfer transition, and the 550 nm band is due to the $5d_{z2}$-$6p_z$ transition in the central metal. Both bands of $Pt(dpg)_2$ abruptly shift to longer wavelength region with increasing pressure [1]. Then, the color of the thin film of $Pt(dpg)_2$ turns from red-brown, to brown, green, greenish yellow and yellow according to the pressure shift of the absorption band.

We have in situ observed the effects of shear stress and pressure on the thin film of $Pt(dpg)_2$ in the sapphire-anvil cell under the microscope. The color of the thin film turns from red-brown at ambient pressure to green at 0.4 GPa. Then, one sapphire-anvil is rotated by the applied force at this pressure. We can see the region changed by shear stress with the naked eye. Plate 1 shows a photograph of the thin film of $Pt(dpg)_2$ under shear deformation at 0.4 GPa. The color changes remarkably from green to yellow at the outer part on the anvil, but the color at the center is green.

PLATE 1 Photographs of the thin film of $Pt(dpg)_2$ under shear deformation at 0.4 GPa. The color of the thin film changes remarkably from green to yellow at the outer part, but the color at the center is green. The yellow region is remarkably observed at around about 75% of the radius (0.75 r). (See COLOR PLATE IV)

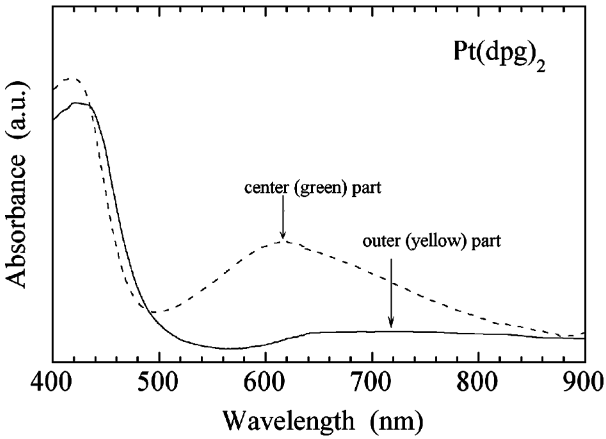

FIGURE 1 Absorption spectra at the center (green) and outer (yellow) parts under shear deformation at 0.4 GPa.

Figure 1 shows the absorption spectra at the center and outer parts. The absorption intensity of the visible band in the outer (yellow) part sharply decreases and this absorption peak rapidly shifts to the near-infrared region. On the other hand, the absorption spectra do not change around the center (green) part. In a previous paper we have reported that the d-p band rapidly shifts to the near-infrared region at

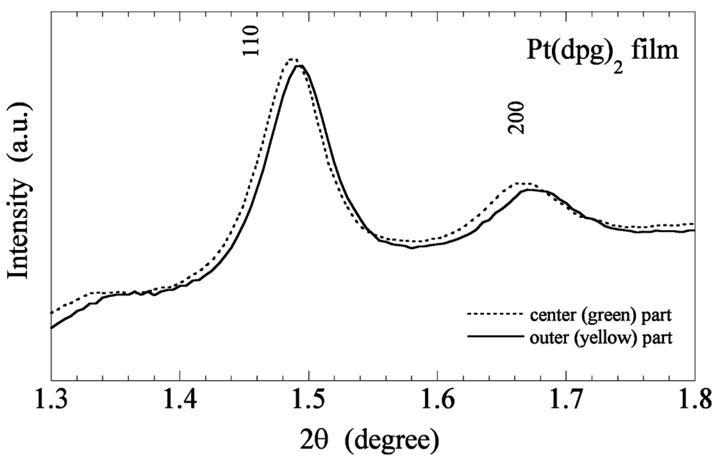

FIGURE 2 Powder x-ray diffraction profiles at center (green) and outer (yellow) parts under shear deformation at 0.8 GPa.

high pressures [1]. Then, the color becomes yellow. This behavior is very similar to the result obtained by the applying shear deformation to the thin film.

Figure 2 shows powder x-ray diffraction profiles of the thin film of $Pt(dpg)_2$ at the center and outer parts under shear deformation at 0.8 GPa. The measurement of the x-ray diffraction in the SDAC must be exposed to synchrotron radiation above two hour. It is very difficult that we observe the diffraction lines in the high-angle region. The 110 and 200 lines at outer part markedly shift to the lower d-value region. Both lines at the center part are insensitive to shear stress. This behavior corresponds to the shift of the absorption peak at outer part. We have also found the interesting shear stress effects on the absorption spectra for the organic thin films like pentacene and tetracene [5].

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