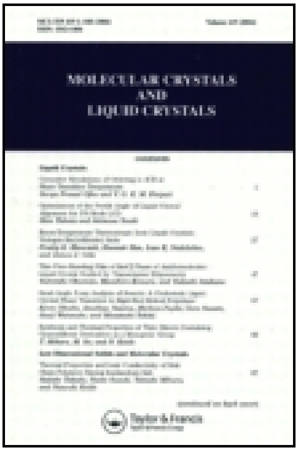

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Electrical Properties of Thin Films of BIS(1,2-Benzoquinone Dioximato)Platinum(II), $Pt(BQD)_2$

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ELECTRICAL PROPERTIES OF THIN FILMS OF BIS(1,2-BENZOQUINONE DIOXIMATO)PLATINUM(II), PT(BQD)$_2$

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Abstract Resistivity, X-ray diffraction and thermal analysis of Pt(bqd)$_2$ were studied. The resistivity of the oriented thin film of this complex was 2×10^3 Ωcm at room temperature and decreased with increasing temperature up to 400 K. After the temperature was reduced to room temperature, the resistivity of the film lowered to 2×10^2 Ωcm. The resistivity dose not return to the original even if the temperature is reduced to room temperature. The small exothermic anomaly was observed at around 350 K in the DSC curve. This may closely be related to the interesting irreversible electrical behavior.

INTRODUCTION

An electrical resistivity of one-dimensional bis(1,2-benzoquinone dioximato)-platinum(II), Pt(bqd)$_2$, rapidly decreases with pressure up to ca. 1.7 GPa, and then increases drastically up to 6 GPa.[1] Recently, the X-ray diffraction of Pt(bqd)$_2$ with synchrotron radiation has been studied at high pressure; the structural anomaly in this complex is observed at around 1.7 Gpa.[2] This structural anomaly is closely related to the interesting electrical behavior at high pressure.

Pt(bqd)$_2$ complex crystallizes in a columnar structure and has the shortest Pt-Pt distance(3.17 Å) in any known d^8-bis(1,2-dione dioximato)platinum(II) compounds.[3] The resistivity of Pt(bqd)$_2$ along the needle axis of a crystal is 3×10^2 Ωcm. The absorption band assigned the d-p transition is observed at around 8000 cm^{-1} for this complex.[4] These values are much lower compared with the analogus d^8 complexes. The electronic states of evaporated thin films of Pt(bqd)$_2$ have already been studied.[5,6] The ionization energy of the thin film of Pt(bqd)$_2$ is 4.96 eV; this value is slightly smaller than that of TTF thin film(5.0 eV).[7]

The resistivity of the oriented film of Pt(bqd)$_2$ is measured to be 6.3×10^4 Ωcm with the thermal energy gap of 0.34 eV in the temperature range from 100 K to room temperature.[6] When the resistivity of the thin film of Pt(bqd)$_2$ was measured from room temperature to 400 K in an atmosphere of argon, the interesting irreversible electrical behavior was found. In this paper we present the results of the resistivity , the thermal analysis and the X-ray diffraction of Pt(bqd)$_2$, and discussed the interesting electrical properties of thin films of this complex.

EXPERIMENTAL

o-Benzoquinone dioxime(o-bqd) was synthesized from commercially available o-nitrosoaniline, which was oxidized with basic NaOCl to give o-nitrosobenzen.[8] Then , it was reduced with basic NH_2OHHCl in ethanol to yield o-bqd. Elemental analysis, IR, NMR and mass spectrometry were used to characterize these compounds in the synthetic processes above. Pt(bqd)$_2$ was prepared by mixing the hot water-ethanol solution containing stoichiometric amounts of K_2PtCl_4 and o-bqd.[5,6] The products were purified by repeated recrystalization from N,N-dimethylformamide or dichlorobenzene.

Thin films of Pt(bqd)$_2$ were prepared by evaporation onto a quartz or a glass substrate held at room temperature in a vacuum(ca. 1.33×10^{-4} Pa). The thickness of the evaporated films was ca. 1000 Å. The X-ray diffraction profiles of Pt(bqd)$_2$ were measured at room temperature using a Rigaku RU-200 B diffractometer with a Cu-Kα radiation source. The electrical resistivity of thin films of Pt(bqd)$_2$ was repeatedly measured 77 K to 400K with the two-prove method in the atmosphere of argon.

RESULTS AND DISCUSSION

The X-ray diffraction study of the single crystal of Pt(bqd)$_2$ has not yet been carried out as the good single crystal is not prepared. Pt(bqd)$_2$ is isostructural with α-Pd(bqd)$_2$. The structure of α-Pd(bqd)$_2$ is orthorhombic, space group Imcb.[9] Figure 1 shows the powder X-ray diffraction pattern of Pt(bqd)$_2$. There is no unknown peak in this pattern. The lattice constants obtained from this data was a=20.654 ± 0.003 Å, b= 9.758 ± 0.001 Å, c=6.360 ± 0.001 Å (needle axis). Figure 2 shows X-ray diffraction profile of the thin film of Pt(bqd)$_2$ at room temperature. Sharp harmonic diffraction lines assigned to the (2n 00)(n=1-6) reflections were observed. The complex molecules are arranged along the a-axis perpendicular to the substrate. The crystal data of Pt(bqd)$_2$ are given in

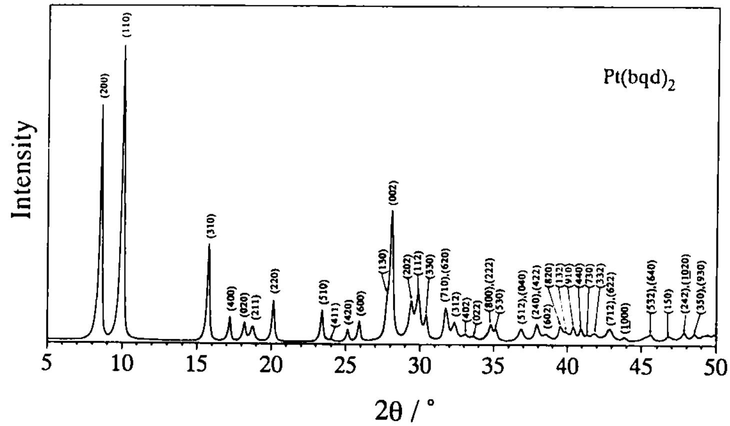

FIGURE 1 Powder X-ray diffraction pattern of Pt(bqd)2 at room temperature

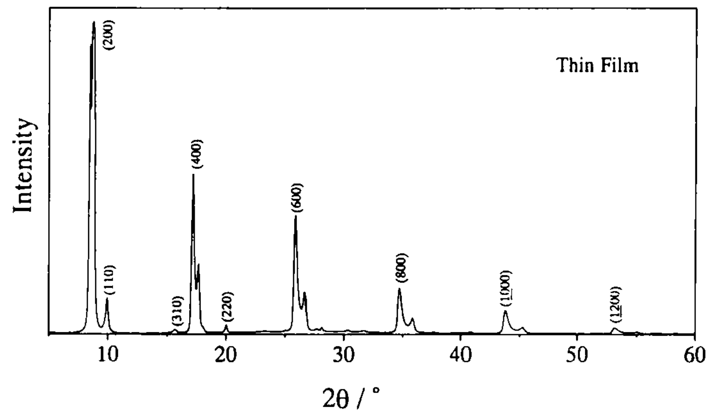

FIGURE 2 X-ray diffraction pattern of the thin film of Pt(bqd)2 at room temperature

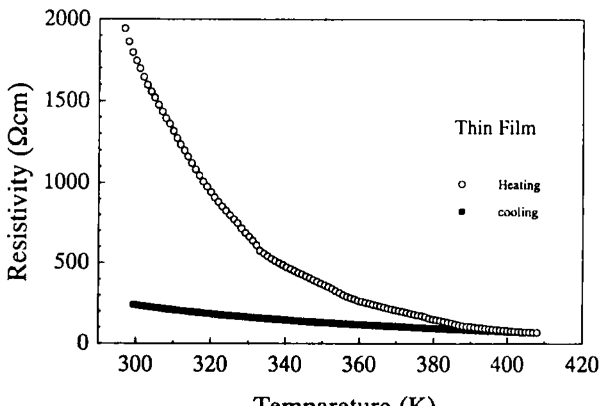

FIGURE 3 Resistivity of the oriented thin film of Pt(bqd)2 at high temperatures

Table 1.

Belombe has measured the electrical conductivity of the single crystal of $Pt(bqd)_2$ from 77 K to 550 K; the conductivity changes rapidly at around 380 K.[3] We have studied the resistivity of the crystal and the oriented thin film of $Pt(bqd)_2$ at high temperatures. The resistivities of several thin films were between 2×10^3 and 6×10^4 Ωcm at room temperature. Figure 3 shows the resistivity of the thin film of $Pt(bqd)_2$ from room temperature to 400 K. The resistivity of 2×10^3 Ωcm at room temperature decreased with increasing temperature up to 400 K. After the temperature was reduced to room temperature , the resistivity of the film lowered to 2×10^2 Ωcm at room temperature. The resistivity dose not return to the original even if the temperature is lowered. The similar electrical behavior at high temperatures was also found for the crystal of $Pt(bqd)_2$. The electrical anomaly at around 380 K reported by Belombe was not observed in the electrical resistivity vs. temperature curves of the thin film and the crystal.

The powder of $Pt(bqd)_2$ was heated to 400 K in an atmosphere of argon and then cooled to room temperature($Pt(bqd)_2$ heated). Figure 4 shows the powder X-ray diffraction pattern of this complex at room temperature. This was very similar to the pattern shown in Fig. 1. However, the intensity of (2n 00) lines increased markedly. This is due to the preferred orientation in the polycrystal by heating. The lattice parameters of $Pt(bqd)_2$ heated are a = 20.624 ± 0.004, b = 9.741 ± 0.002 and c = 6.350 ± 0.002 Å, being slightly shorter than those of the original values. The X-ray diffraction of this film heated up to 400 K was studied at room temperature. This pattern of this film agreed with the profile shown in Fig. 2. Sharp harmonic diffraction lines were also observed. The a-axis of the film is slightly shorter than that of the ordinary film. The resistivity of the thin film heated was measured at low temperatures. The resistivity of the film was 2×10^2 Ωcm at room temperature, and increased with decreasing temperature. The thermal energy gap was ca. 0.17 eV. This value was much smaller than that of the ordinary oriented film which was not heated.

Differential thermal analysis of $Pt(bqd)_2$ was carried out in the atmosphere of argon. Figure 5 shows the DSC of $Pt(bqd)_2$ from room temperature to 420 K. The small exothermic anomaly was observed at around 350 K. This is closely related to the irreversible electrical behavior.

$Pt(bqd)_2$ is a square planar complex which is surrounded by four nitrogen atoms

TABLE 1 Crystal data, resistivity and energy gap of both thin films of $Pt(bqd)_2$ and $Pt(bqd)_2$ heated

	Crystal data				Resistivity	Energy gap
	a (Å)	b(Å)	c(Å)	V(Å^3)	(Ωcm)	(eV)
$Pt(bqd)_2$	20.654 (20.684)	9.758	6.360	1281.9	2×10^3	0.34
$Pt(bqd)_2$ heated	20.624 (20.641)	9.741	6.350	1275.8	2×10^2	0.17

( ) : thin film

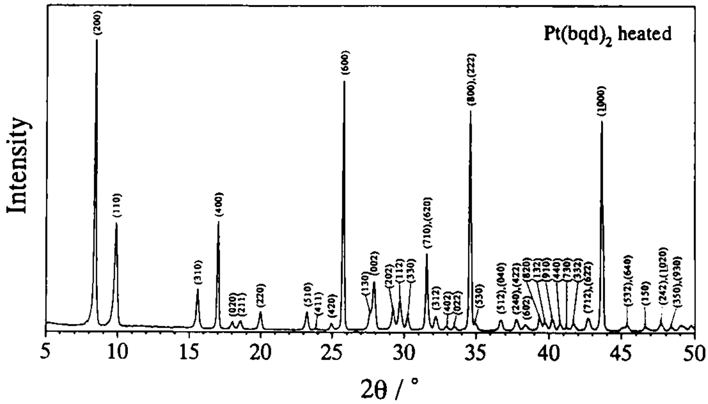

FIGURE 4 Powder X-ray diffraction pattern of $Pt(bqd)_2$ heated

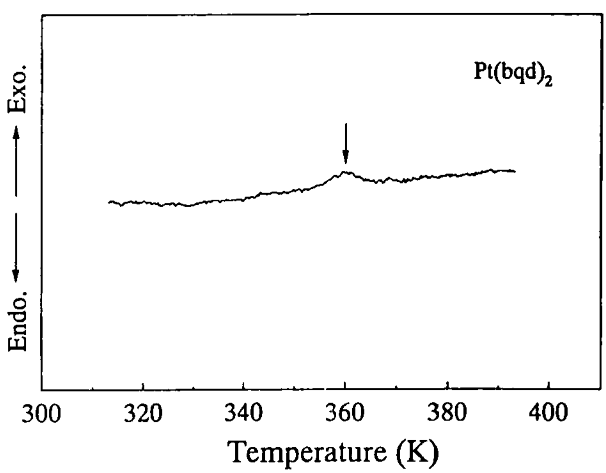

FIGURE 5 DSC curve of $Pt(bqd)_2$ at high temperatures

of two 1,2-benzoquinone dioxime anions. The d orbitals of the Pt^{2+} ion are split by a crystal field of D_{4h} symmetry. The 8 electrons of the Pt^{2+} ion core fill the d_{z^2}, d_{xy}, d_{yz} and d_{zx} states. The complex crystallizes in columnar structures. The columns are formed by square planar complex molecules with the considerably short Pt-Pt distance of 3.17 Å in a direction of stacks. The overlap of the d_{z^2} orbitals can, thus, be produced a valence band that is completely filled. This band is separated from the next empty conduction band formed by p_z orbitals. The intrinsic energy gaps obtained from UPS and absorption spectra of $Pt(bqd)_2$ are 0.84 eV and 0. 99 eV, respectively.[6]

The crystal data, the resistivities and the thermal energy gaps of $Pt(bqd)_2$ and $Pt(bqd)_2$ heated are summarized in Table 1. The resistivity of the thin film heated is 1/10 of the ordinary thin film. The thermal energy gap of this film is ca. 0.17 eV. This value is much smaller than the intrinsic energy gap of $Pt(bqd)_2$. Thus, the $Pt(bqd)_2$ heated may be an extrinsic semiconductor. The lattice constants of $Pt(bqd)_2$ heated are slightly smaller than those of the original. The exothermic anomaly is observed at around 350 K. These results suggest that a very small amount of the hydrogen atoms involved in hydrogen bonding in a $Pt(bqd)_2$ molecules may be removed. Lack of a hydrogen atom can lead to the oxidation state of central platinum cation(from Pt(II) to Pt(III)). This might act as an impurity level. The thin film heated of $Pt(bqd)_2$ may behave as an extrinsic semiconductor. However, we can prepared the conducting thin film of $Pt(bqd)_2$.

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