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Electrical resistivity of a novel oxadiazole derivative as a function of pressure and temperature using a diamond anvil cell*

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The *in-situ* electrical resistance measurement on the microcrystal of 1,4-bis[(4-methyloxyphenyl)-1,3,4-oxadiazolyl]-2,5-bisheptyloxyphenylene (OXD-2) has been carried out under conditions of high pressure and temperatures higher than room temperature by using the diamond anvil cell (DAC). The sample's resistivity was calculated with a finite element analysis method. The temperature and pressure dependencies of the resistivity of OXD-2 microcrystal were measured up to 150°C and 16GPa. The resistivity of OXD-2 decreases with increasing temperature, indicating that OXD-2 exhibits organic-semiconductor conducting property in the region of experimental pressure. Between 90–100°C, the resistivity drops with the temperature, which reveals a temperature-induced phase transition. As the pressure increases, the resistivity of OXD-2 increases and reaches a maximum at about 6 GPa, and then begins to decrease at higher pressures. Combining the *in-situ* x-ray diffraction data with the resistivity measurement under pressure, the anomaly resistivity drop after 6 GPa is confirmed to be due to the pressure-induced amorphous phase transition of OXD-2.

Keywords: resistivity measurement, high pressure, oxadiazole
PACC: 7280L, 0735, 7200, 6110

1. Introduction

The design and fabrication of efficient light emitting devices (LEDs) based on organic materials have been the active research area due to their possible applications in the low-cost, large area display technology.[1−5] 1, 3, 4-oxadiazoles are one of the most widely studied classes of organic electron-transport materials and are proven to be effective electron-transport agents in LEDs.[6−8] The first oxadiazole derivative that has been successfully applied in OLED is 2-(-biphenyl)-5-(4-tert-butylphenyl)-1, 3, 4-oxadiazole (PBD).[9] After wards, various kinds of oxadiazole molecules have been used to obtain high electroluminescence (EL) performances, such as bisoxadiazoles,[10] branched or dendrimeric oxadiazoles,[11] and polymers containing oxadiazole units either in the main chain [12−15] or in the side chain.[16−18] Additionally, they have extremely high stability to thermal and oxidative degradation. To obtain more effective LEDs, we should know the electron transport mechanism of these organic materials. Since pressure and temperature can easily modify the crystal environment and make the electron transport phenomenon more prominent, we believe that electrical measurement under high pressure and temperature conditions are helpful to understand the electron transport mechanism. The high pressure effect just as the temperature effect on the properties of functional materials has been a subject of numerous investigations in the past few years due to the developments of the high pressure generation technology and the de-

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tecting methods.[19−21]

This paper reports a novel quasi four-probe resistivity measurement on a 1, 3, 4-oxadiazole derivative microcrystal in diamond anvil cell (DAC). We directly use the finite element analysis to calculate the sample resistivity. In this paper, we mainly focus our investigation on the resistivity of OXD-2 as a function of temperature and pressure.

2. Experiment

The oxadiazole derivative OXD-2 was synthesized by cyclocondensation of diahydrazides and recrystallized from ethanol. The microcrystal sample was provided by Key Laboratory for Automobile Materials, Ministry of Education, Department of Materials Science, Jilin University.

The high-pressure x-ray diffraction experiments were carried out in DAC at room temperature on a BRUKER three-circle diffractometer with a SMART APEX 4 K CCD area detector. Mo $K\alpha$ radiation (λ=0.071073nm) monochromatized by a graphite crystal was used as the incident ray. The x-ray diffraction data were treated with Materials Studio (MS) from Accelrys Inc.

In our experiment, the resistivity measurement under high pressure was performed with DAC onto which thin film electrodes and protective layer were integrated. Molybdenum was selected as the materials of metallic microcircuits, and then was sputtered onto a clean diamond anvil. The Mo film thickness was around 300.0nm. As shown in Fig.1, Mo thin film was patterned into a quasi four-probe arrangement. After patterning the Mo film into designed circuits, a hard insulating Al_2O_3 layer with a thickness of 2μm was also sputtered onto Mo-film-coated diamond anvil to prevent the metallic probes from breaking at the edge of culet under high pressure. Previous experiment proved that Al_2O_3 could provide reliable insulation between the metal microcircuits and metal gasket even under pressures exceeding 200GPa.[22] For a better insulation, 2-μm-thick Al_2O_3 layer was also sputtered onto the preindented T301 stainless steel gasket. Other experimental details have been presented in Ref.[23]. Since metal probes under insulating layer could contact with the sample, partial Al_2O_3 layer on the central culet was removed chemically, and consequently, a rectangular detecting window was formed and two pieces of electrodes were exposed. The exposed electrodes not only provided the current but also served as terminals for voltage drop recording. With this designed diamond anvil, the conducting property of OXD-2 was investigated under variable temperature and pressure conditions. Temperatures were measured by using a nickel chromium–nickel silicon thermocouple in close proximity to anvils.

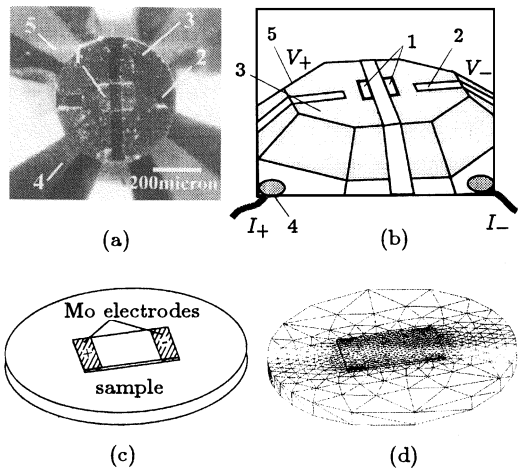


Fig.1. Configuration of a microcircuit on a diamond anvil and schematic diagram of FEA in dc-current field simulations. (This figure is in colour only in electronic version). (a) The configuration of a complete microcircuit. 1. exposed Mo electrode; 2. exposed diamond anvil; 3. Al_2O_3 layer on the Mo above the electrode; 4. connection to current supply. V_+, V_-, I_+, and I_- denote the positive and negative voltage and current ends in the circuit. (b) A photograph of the circuited diamond anvil in correspondence with (a). (c) A model in FEA simulation. (d) The model meshed by elements.

Due to the regular shape and fixed position of the electrodes in DAC, the resistivity of the sample could be calculated accurately under high pressure by the finite element analysis (FEA) method that has demonstrated very high performance in steady electric conduction simulation. Resistivity calculation by FEA consisted of two principal parts of work, the modelling and the simulating. In the modelling procedure, all parameters input into FEA were identical with those in real electrical measurements, such as the sample dimension, the electrode dimension and position, the electrode resistivity, and the electric current. Meanwhile, a trial sample resistivity was also needed to input into FEA for successive simulation. With these parameters, a voltage drop between electrodes could be obtained through FEA simulation. When the simulated voltage drop was equal to the measured one, the trial sample resistivity was just the actual resistivity we wanted. To perform simulation exactly, the sample thickness needed to be measured *in situ*.

3. Results

Figures 2(a) and 2(b) show the temperature dependence of resistivity of OXD-2 at pressures below and above 6.8GPa, respectively. Because of the limitation by the measuring range of our experimental instruments, the resistance at temperatures lower than 70°C cannot be exactly recorded. Therefore, the resistivities are measured at a higher temperature range (70–150°C). As shown in Fig.2, the resistivity of OXD-2 decreases from $10^6\Omega\cdot$cm to $10^4\Omega\cdot$cm as the temperature increases, so we can conclude that OXD-2 exhibits an organic semiconductor conducting property in the entire pressure range of the experiment. The decrease of resistivity with increasing temperature results from the enhanced thermal excitations that can lead to the increase of π-electron delocalization and can make the electron transport between molecules more easily. At about 90°C, the resistivity drops sharply with increasing temperature, which may be caused by a temperature-induced phase transition, and this new phase is in favour of electron transport. The abrupt drop of OXD-2 resistivity at about 90°C becomes weak with increasing pressure, because the pressure restrains the temperature-induced phase transition. In Fig.2(b) the inset shows the pressure dependence of OXD-2 resistivity at 80°C. It can be seen that during compression the OXD-2 resistivity increases at below 6GPa and drops a lot at higher pressures. Succeeding x-ray diffraction proves that the structural change in OXD-2 microcrystals would give rise to the anomaly of resistivity variation under high pressures.

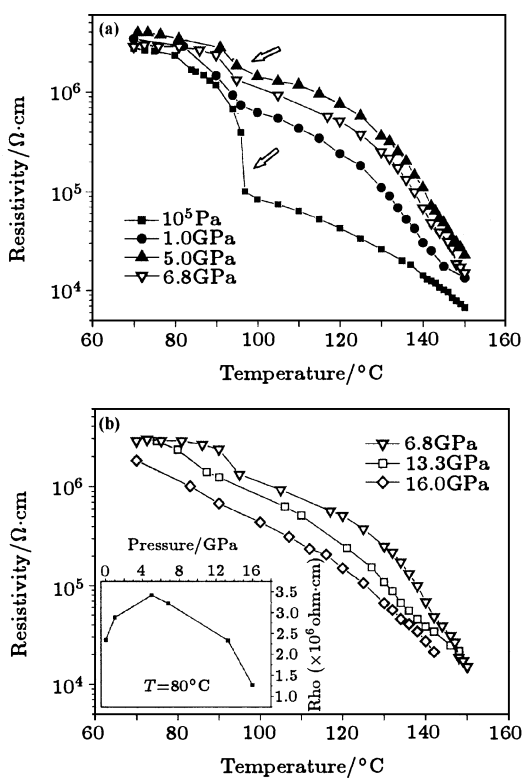


Fig.2. Temperature dependence of electrical resistivity of OXD-2. (a) At pressures below 6.8GPa; (b) At pressures above 6.8GPa. The inset: pressure versus electrical resistivity of OXD-2 at 80°C.

Since the basic effect of pressure is to decrease the volume of materials, it leads to structural transformation and the change of overall electron transport behaviour in materials. Figure 3(a) presents the powder x-ray diffraction pattern of OXD-2 at 1×10^5Pa. OXD-2 belongs to the orthorhombic system, $P2_12_12_1$ space group with a=2.7291(7)nm, b=2.5660(4)nm, c=0.4736(5)nm. Figure 3(b) shows the x-ray diffraction patterns at different pressures. The shifts of diffraction peaks to higher angles indicate that the interplanar distance decreases with pressure.

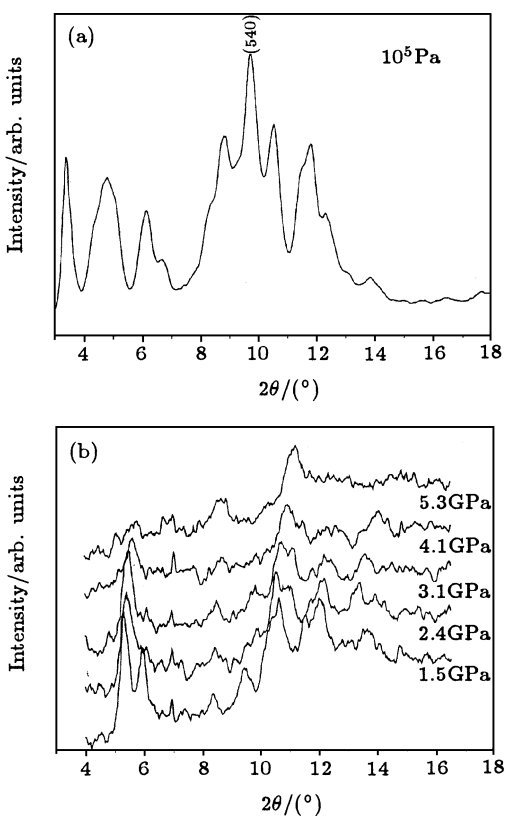


Fig.3. (a) Powder x-ray diffraction pattern of OXD-2 at ambient pressure. (b) Powder x-ray diffraction patterns of OXD-2 in DAC at high pressures.

In DAC, very few main x-ray diffraction peaks can be identified in the experiment. It is hard to obtain a reliable characterization about the crystal structure only by the few main peaks, but the shifts of different diffraction peaks still can be reflected by the shift of only one peak, such as the shift of $d_{(540)}$. Figure 4

presents the change of $d_{(540)}$ value against pressure. The continuous decrease of d with pressure and the x-ray patterns in Fig.3(b) imply that there is no phase transition in OXD-2 below 6GPa. When the pressure becomes higher than 6GPa, all of the diffraction peaks disappear, indicating that OXD-2 transforms to an amorphous phase.

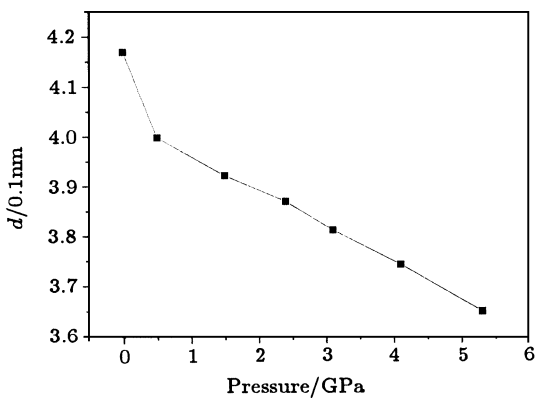


Fig.4. Variation of $d_{(540)}$ of OXD-2 against pressure.

Therefore, by analysing the x-ray diffraction data, we can conclude that the resistivity drop of OXD-2 at above 6GPa is caused by the amorphous transformation under high pressure. For the crystalline phase of OXD-2 shown in Fig.2(b), its resistivity variation with pressure can be attributed to two aspects: on the one hand, the band gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) narrows with increasing pressure,[24,25] causing the carriers being transported across the band gap more easily, and thus the resistivity decreases. On the other hand, the crystal lattice defects increase during compression, which hinder the electrons from transporting, causing the resistivity to increase. The latter effect is stronger than the former, thus leading to the increase of overall resistivity at pressures below 6GPa. Upon further application of pressure, OXD-2 becomes amorphous phase, the lattice defects vanish and only the former effect works, so the resistivity decreases with pressure.

4. Conclusion

In summary, by using thin-film probes integrated techniques in DAC, we have performed electrical measurements on a novel 1,3,4-oxadiazole derivative under variable pressure and temperature conditions. With the finite element analysis, sample resistivities are obtained accurately. The temperature dependence of resistivity indicates that the OXD-2 exhibits semiconductor conducting behaviour within the range of experimental pressure and that there is a temperature-induced phase transition; however, with increasing pressure, this phase transition is restrained. The pressure dependence of resistivity reflects the amorphous transition of OXD-2 at around 6GPa. From the above results, we think that for the crystalline phase of OXD-2, the electron transport is primarily affected by the defects in the crystal lattice, while for the amorphous phase, electrical transport behaviour is primarily affected by the band gap.

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