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Effects of high pressure on the Raman and fluorescence emission spectra of two novel 1,3,4-oxadiazole derivatives*

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The effects of pressure on the fluorescence emission and Raman spectra of 1,4-bis[(4-methyloxyphenyl)-1,3,4-oxadiazolyl]- 2,5-bisheptyloxyphenylene (OXD-2) and on the fluorescence emission spectra of 1,4-bis[(4-methylphenyl)-1,3,4-oxadiazolyl]phenylene (OXD-1) are investigated using a diamond anvil cell. With the increase of pressure, the intensity of the fluorescence emission increases and reaches maxima at 13GPa for OXD-1 and at 9.6GPa for OXD-2. The effect of pressure on the peak position of the emission shows a similar trend, red shift with the increase of pressure. But at higher pressures, the intensity of emission drops down dramatically. The Raman spectra of OXD-2 indicate that there appears a structural change at ca 3GPa.

Keywords: high pressure, oxadiazole, fluorescence, Raman
PACC: 0735, 7830J, 3350D

1. Introduction

Recently one is increasingly interested in an aromatically substituted oxadiazole in the sense of new high-tech materials for devices such as sensor technology, non-linear optical application, new batteries and other electrical and electronic technologies, etc.[1−7] All kinds of interesting properties need to be adjusted to actual requirements in a wide range by different chemical and physical techniques. High pressure effects on the properties of functional materials have been a subject of numerous investigations in the past years due to developments of the high pressure generation technology and detecting methods. The most important effect of hydrostatic pressure is the decrease in material volume and the increase in intermolecular interaction. And all chemical and physical properties depend on the interactions among the outer electronic orbitals. So the pressure is an important tool to modify properties of materials. The studies of the pressure dependence of the Raman spectra of molecular crystals have shown that vibrational frequency shifts are related to the perturbations of inter- and intramolecular interactions by pressure. Fluorescence emission under pressure is a valuable tool in estimating the interchain coupling by observing the changes of intensity and wavelength shift. It is evident that a combined study of the pressure-induced fluorescence and Raman shifts is likely to give a greater insight into pressure-induced changes in the intra- and intermolecular interactions.[8]

In the paper, we study two novel 1,3,4-oxadiazole derivatives, new conjugated oligomers with an alternating phenylene-oxadiazole structure. They have potential applications in electro-luminescent devices. In general, the photo-induced luminescence is a fundamental aspect for the electro-luminescent materials. Thus we have investigated the effects of pressure on

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the fluorescence emission as well as the Raman spectra of OXD-2, and fluorescence emission spectra of OXD-1. A combined study of fluorescence and Raman under pressure is performed to prove reciprocity between the change of property and intermolecular interaction.

2. Experiment

The oxadiazole derivatives OXD-1 and OXD-2, which are synthesized by cyclocondensation of diahydrazides, were supplied by Key Laboratory for Automobile Materials, Ministry of Education, Department of Materials Science, Jilin University. They are white powder, recrystallized from ethanol.

High pressure was generated in a diamond anvil cell. The hole diameter of the gasket to hold the sample was ca 300μm with a thickness of ca 150μm. Light mineral oil served as a pressure medium in fluorescence measurement. The 4:1 methanol-ethanol mixture was used as a pressure medium for Raman measurement. The pressure was measured by the well-known ruby fluorescence technique. The fluorescence spectra were recorded using SPEX-1403 with 488.0nm Ar laser. Raman spectra with the diamond cell were recorded in a backscattering mode, using JY-HR800 spectrograph with an air cool CCD detector. The Raman spectra were excited by a He–Ne laser (632.8nm).

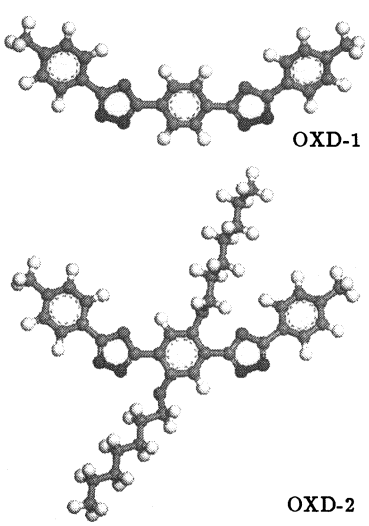


Fig.1. Molecular structures of OXD-1 and OXD-2.

3. Results and discussion

The molecular structures of OXD-1 and OXD-2 are showed in Fig.1. Under an excitation at a wavelength of 488.0nm at ambient pressure, OXD-1 emits fluorescence. The emission peak is attributed to $\pi-\pi^*$ transition. But at ambient pressure, the 488.0nm excitation line cannot excite OXD-2. With the increase of pressure to above 4 GPa, OXD-2 begins to emit fluorescence. The effect of pressure on the peak position of the emission is showed in Fig.2. The fluorescence wavelengths increase with pressure almost linearly, but the slopes are different. The pressure coefficients are 1cm-1/GPa for OXD-1 and 8cm-1/GPa for OXD-2, respectively. The oxadiazole is electron deficient moiety, and introduction of two alkoxy groups, whose electron-donating ability is strong, increases the electron density of the conjugated segment of OXD-2. Under the pressure, the electronic π-orbital overlap of OXD-2 increases so significantly that the pressure coefficients are different for the two oligmers. However, that may be due to the different spacings between molecular planes resulting from the different compressibility.

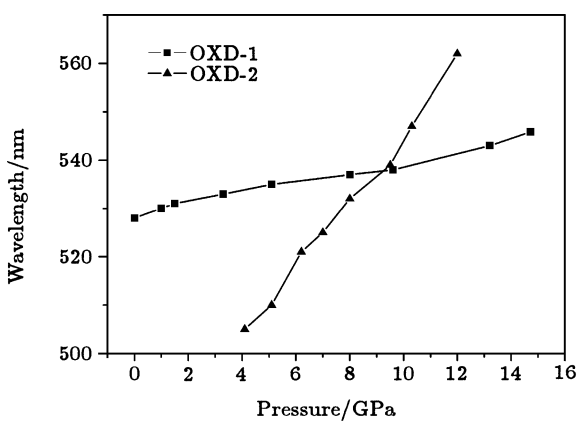


Fig.2. Oxdiazole derivation fluorescence shifts vs pressure.

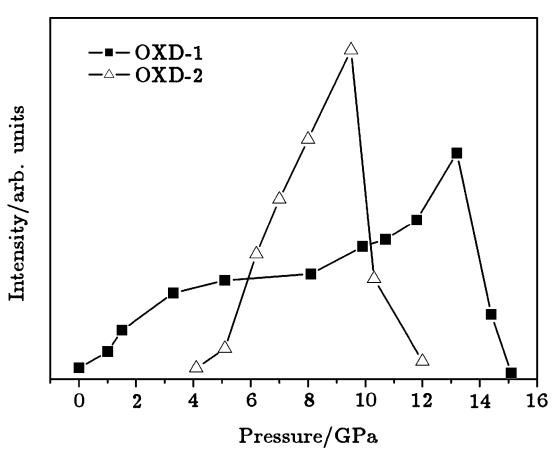


Fig.3. Fluorescence peak intensity of oxadiazole derivation shift vs pressure.

It can be seen in Fig.3 that with the increase of pressure the intensities of the emission are enhanced and reach maxima at 13GPa for OXD-1 and

at 9.6GPa for OXD-2, and drop down a lot at higher pressures. The pressure decreases the intermolecular distance, but increases the intermolecular $\pi-\pi^*$ interaction thus reduces the band gaps. When the pressure reaches 4GPa, the band gap of OXD-2 is so narrow that OXD-2 can be excited. At 9.6GPa, the band gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital is 2.54eV. The efficiency of 488.0nm excitation reaches a maximum, so the intensity of emission arrives at a maximum, too. While the pressure is higher, the smaller the band gap, the easier the internal conversion is achieved, and the lower the luminescent efficiency becomes.[8] OXD-1 has the same trend.

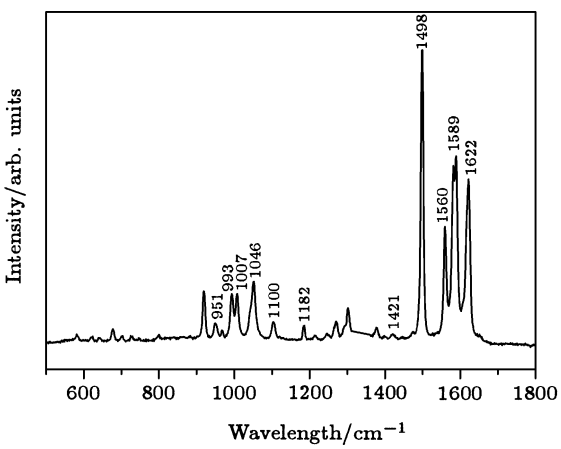


Fig.4. Raman shift of OXD-2 at ambient pressure.

Figure 4 shows the Raman spectrum of OXD-2 in a region between 500 and 1800cm^{-1} at room temperature and at ambient pressure. The Raman spectrum of OXD-1 is submerged by strong fluorescence. The assignment to the different modes is done using data for 1,3,4-oxadiazoles from Refs.[9–11] and also from Raman investigations of different dipheny-1,3,4-oxadiazole derivatives.[12] The spectra are all from internal lattice vibrations. The most prominent vibrations at 1589 and 1622cm^{-1} are attributed to ring vibrations of the phenyl rings, while the oxadiazole rings are responsible for 1498 and 1560cm^{-1}. The additional vibrations at 951, 1007, 1182, 1421cm^{-1} originate from all oxadiazole ring modes but with lower intensities. The mode at 993cm^{-1} should be due to the diaryl-substituted oxadiazole with two other characteristic frequencies at 1046 and 1100cm^{-1} according to Ref.[13]. The other lines with minor intensities found in the spectrum may also be assigned to ring vibrations mainly of the phenyl rings.

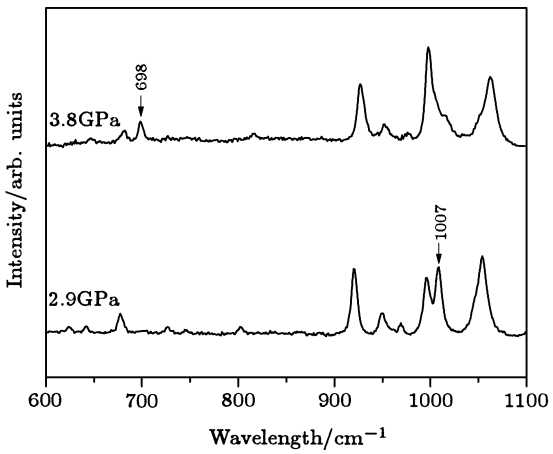


Fig.5. Observed Raman peak shifts of OXD-2 at ca 3GPa.

The pressure dependence of all Raman mode frequencies is investigated with 632.8nm excitation lines. As showed in Fig.5, an important feature of the Raman spectra under a pressure of ca 3GPa is the disappearance of a peak at 1007cm^{-1} and appearance of a peak at 698cm^{-1}, which is presumed to be due to the pressure. We can expect the initial effect of pressure to reduce the intermolecular space without significantly affecting the intermolecular interaction. By further increasing pressure the interchain coupling becomes a dominant factor. The molecules begin to feel the stronger intermolecular interactions, which may be due to the interaction between different ring vibrations or C–H motions resulting in distortion of ring planarity or deformation in the carbon backbone structure. So, frequency shifts or mode splitting may occur; some lines may disappear but new ones occur. Raman spectra cannot be obtained under pressures above 12GPa in the case of OXD-2, because of its strong interference from fluorescence that shifts to a range of Raman spectra with pressure increasing. The pressure-induced shifts are absolutely reversible. The modes at 698 and 1007cm^{-1} changing with pressure is an additional indication of the effect of interchain interactions, which fully supports the interpretation in the description of fluorescence spectra.

4. Conclusions

The two new conjugated oligomers with an alternating phenylene–oxadiazole structure are studied at high pressures. The fluorescence emission and Raman spectra under high pressures turn out to be consistent with the determining of the effect of intermolecular interaction. With pressure increasing, the electronic

π-orbital overlap and the interchain coupling increase but the band gap decreases. With pressure decreasing, these changes are reversible. There still remain some problems unsolved, and we will further study the oxadiazole derivatives in future.

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