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Yuanyuan Hou[1]**, Bingbing Liu**[1]**, Lin Wang**[1]**, Shidan Yu**[1]**,**
Mingguang Yao[1]**, Ao Chen**[1]**, Dedi Liu**[1]**, Yonggang Zou**[1]**, Zepeng Li**[1]**,**
Bo Zou[1]**, Tian Cui**[1]**, Guangtian Zou**[1]**, Agnieszka Iwasiewicz-Wabnig**[2] **and**
Bertil Sundqvist[2]

[1] National Lab of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China
[2] Department of Physics, Umeå University, S-90187 Umeå, Sweden

E-mail: lliubb@jlu.edu.cn

Abstract
In this paper, we report a comparative study of pressure-induced polymerization in C_{60} nanorods and bulk single crystals, treated simultaneously under various pressures and temperatures in the same experiment. For both materials, orthorhombic, tetragonal and rhombohedral phases have been produced under high pressure and high temperature. The structures have been identified and compared between the two sample types by Raman and photoluminescence spectroscopy. There are differences between the Raman and photoluminescence spectra from the two types of materials for all polymeric phases, but especially for the tetragonal phase. From the comparison between nanorods and bulk samples, we tentatively assign photoluminescence peaks for various polymeric phases.

1. Introduction

Recently, one-dimensional C_{60} nanostructures, such as wires, rods and tubes, have attracted much attention due to their potential applications in nanoscale devices [1–8]. The synthesis of highly crystalline C_{60} nanorods with various structures is of great interest in this field. Recently, we found a very simple and effective method, in which individual C_{60} nanorods with widths and thicknesses of the order of nanometers can be rapidly grown with m-xylene as a shape controller. The nanorods can easily grow on various substrates. Nanorods with different diameters and length-to-diameter ratios can be synthesized under different growth conditions. The nanorods that are obtained are highly crystalline and single face-centered cubic (fcc) phase, and a lattice expansion was found in the C_{60} nanorods as their widths decreased [1]. We find that it is very interesting and important to investigate their structural and physical properties. It is well known that C_{60} fullerene can be polymerized through $[2 + 2]$ cyclo-addition of double

bonds under light irradiation or pressure. Under high-pressure and high-temperature (HPHT) conditions, dimers (D), one-dimensional orthorhombic (O), and two-dimensional tetragonal (T) and rhombohedral (R) phases have been prepared [9–19]. Usually, the polymeric structures of C_{60} samples are sensitive to the HPHT environment, i.e. they depend on pressure, temperature, treatment path and even treatment time. To identify any differences between nanorods and bulk samples, one must eliminate effects caused by changes in the treatment condition or differences in treatment times. Therefore, it is important to investigate the structure of C_{60} nanorods and bulk single crystals treated under the same conditions and for the same time.

Recently, optical studies of the polymeric phases also revealed differences between the photoluminescence (PL) spectra of pristine C_{60} and its polymeric forms [20–27]. There is only a small number of published works about the PL for polymeric bulk C_{60}, and the assignment of the PL peaks for each polymeric phase is still unclear [22–25]. Venkateswaran *et al* [24] reported two broad PL peaks at 1.65 and 1.50 eV, but they did not give any assignments of the peaks. Meletov *et al* [25] reported that the T phase has two main peaks: a weak one at 1.534 eV and a stronger one at 1.437 eV. They assigned 1.534 eV as the energy gap for the T phase of bulk C_{60}. We previously found that the main PL peak for the O phase of C_{60} nanorods is at 1.657 eV and that the main peak of the T phase of C_{60} nanorods is at 1.588 eV [27]. It is obvious that the assignment of the PL peaks for the polymeric phases is still in dispute due to the different results obtained in PL studies on polymeric C_{60} nanorods and bulk samples. However, we cannot rule out that these differences arise from different treatment conditions in experiments by different groups. Therefore, it is also necessary to study whether there are any differences between the PL spectra of C_{60} nanorods and bulk single crystals transformed into various polymeric phases under identical HPHT conditions.

In this paper, we report a comparative study of pressure-induced polymerization of C_{60} nanorods and bulk single crystals under various pressures and temperatures in the same experiments. The orthorhombic, tetragonal and rhombohedral polymeric phases have been obtained. Raman and PL spectra from nanorods and single crystals have been compared in detail, and we find differences between the two types of materials, especially for the tetragonal phase. In addition to this comparison between nanorods and bulk samples, we tentatively assign some previously unclear photoluminescence peaks to various polymeric phases.

2. Experimental details

C_{60} nanorods with widths of 200–300 nm were grown by a liquid solution evaporation method, using a C_{60} powder of a nominal purity of 99.9% as raw material. C_{60} nanorods were grown by slowly evaporating the solution on metallic Mo substrates. X-ray diffraction showed that the pristine rods had an fcc structure [1].

In the high-pressure polymerization work, C_{60} nanorods and bulk single-crystal samples were polymerized together under quasi-hydrostatic high-pressure conditions, using two kinds of high-pressure apparatus to obtain three different phases. To obtain the O and T phases, the samples were treated under truly hydrostatic conditions in a piston–cylinder device with silicone oil as the pressure medium, and to obtain the R phase they were treated under higher pressure and temperature using a 6×600 ton cubic high-pressure apparatus with an electric current heating device and vaseline as the pressure medium. From previous studies of polymerization in bulk C_{60} samples it is well known that heating before pressurization will give more pure polymeric phases [10], and to produce the O and T phase samples were thus heated to the final temperature before final pressurization. The final conditions for the O and T phases were 1.5 GPa, 573 K and 2 GPa, 700 K, respectively. However, for the R phase, the samples were treated using a pressing-then-heating procedure due to limitations of the cubic
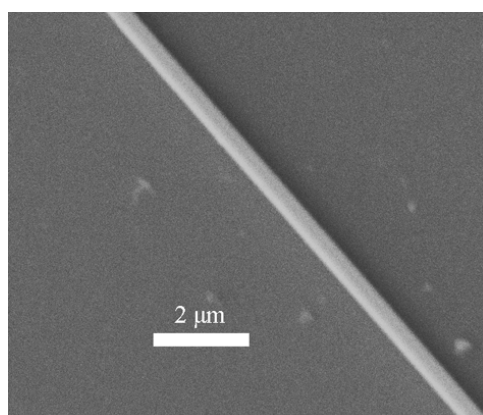
Figure 1. SEM image of an as-grown C_{60} nanorod.

high-pressure apparatus, and we used micrometer C_{60} rods instead of bulk single crystals under R phase conditions due to the space limits of the sample cell. The samples were first pressed to 4.5 GPa, then heated to 973 K, under which conditions the R phase is usually formed in bulk C_{60}. The polymeric samples of C_{60} nanorods and bulk single crystals were washed with pentane and aether several times after the pressure run.

Raman spectra and photoluminescence spectra were measured with a Renishaw inVia Raman spectrometer at room temperature, using a CCD detector to measure light intensities. In order to collect the scattered light from a single C_{60} nanorod, a $100\times$ objective lens was used. The beam of the exciting argon ion laser ($\lambda = 514$ nm) was focused on a 0.5 μm spot and the irradiation power was less than 0.2 mW. Scanning electron microscopy (SEM, SSX-550) was used to observe the morphology of C_{60} nanorods.

3. Results and discussion

A typical SEM image of an as-grown sample deposited on a Mo substrate is shown in figure 1. It is obvious that the sample is in the shape of a rod with a width of several hundred nanometers. The majority of the nanorods have a width of 200–300 nm, and the average length is of the order of several micrometers [1]. From previous studies we know that the shape of the nanorod is preserved during quasi-hydrostatic pressure treatment [26, 27] and that HPHT treatment is a powerful tool for obtaining various new structures in C_{60} nanorods.

Typical Raman spectra for C_{60} nanorods and bulk single crystals treated at 1.5 GPa, 573 K are shown in figure 2(a). The figure shows that the $A_g(2)$ mode shifts from 1469 to 1458 cm^{-1} for both types of materials, but the spectra are slightly different for nanorods and bulk single crystals. Most of the Raman modes in polymeric nanorods are broader and weaker than those of polymerized bulk single crystals. It is well known that the Raman spectrum of pristine C_{60} usually contains ten modes: eight with H_g and two with A_g symmetry. The Raman spectrum changes significantly when the C_{60} molecules bond together in different configurations. The intermolecular vibrations are very strongly affected by polymerization, since weak van der Waals interactions are replaced by covalent bonds. In polymeric C_{60} bulk samples, a number of broad or split bands appear, indicating that the symmetry has been reduced [10]. The pentagonal pinch mode $A_g(2)$, normally observed as a peak at 1469 cm^{-1} for pristine monomeric C_{60}, is sensitive to polymerization, and as a consequence its position can
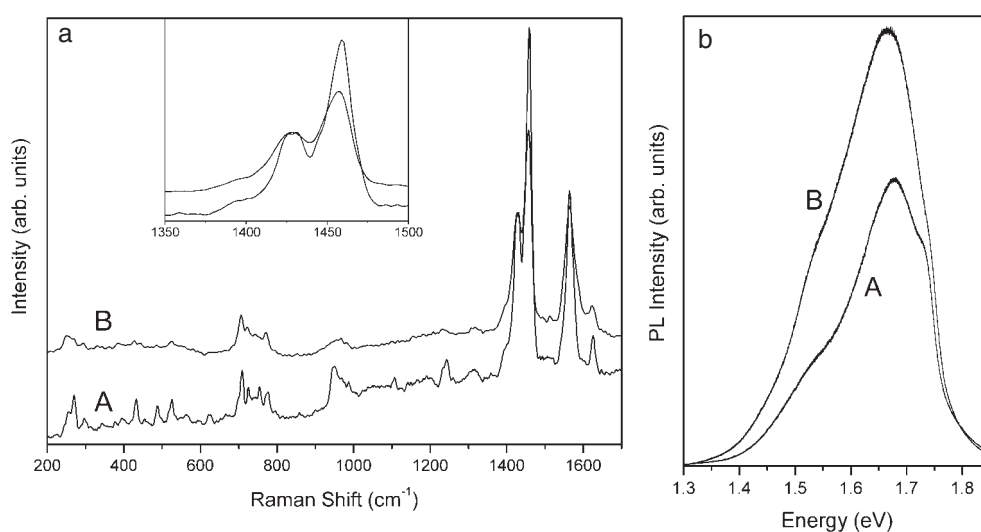
Figure 2. (a) Raman spectra and (b) PL spectra for C_{60} bulk single crystals (A) and C_{60} nanorods (B) treated at 1.5 GPa, 573 K (O phase).

be used as a fingerprint of the polymer lattice structure. The different polymers are usually identified from the shift in the $A_g(2)$ mode because its frequency depends on the number of intermolecular bonds on the molecule. The formation of intermolecular bonds shifts the electron density away from the remaining double bonds, which become weaker. This causes a negative shift in the $A_g(2)$ mode to approximately 1459 cm^{-1} in the O linear chains, to 1447 cm^{-1} in the T structure, and to 1408 cm^{-1} in the R phase for bulk C_{60} [10]. From our experimental data, the characteristic peak at 1458 cm^{-1} indicates that both the C_{60} nanorods and the bulk single crystals have been transformed to the O polymeric phase after treatment at 1.5 GPa, 573 K. The results for these nanorods are similar to those in our previous study [27]. Typical PL spectra for C_{60} nanorods and bulk single crystals in the O phase are shown in figure 2(b). The peak of the fluorescence band was observed at 1.67 eV for the O phase of bulk single crystals, which is very close to the 1.66 eV observed in nanorod samples. The intensity of the PL for bulk single crystals in the O phase is weaker than for the O phase C_{60} nanorod. According to Venkateswaran *et al* [24], two broad PL peaks were observed at 1.65 and 1.50 eV, but they did not give any assignment of these two peaks. From our PL results, we suggest that 1.67 or 1.66 eV should be attributed to the O phase, since the same fluorescence band is observed in both nanorods and bulk single crystals. Other peaks at 1.53 and 1.74 eV, visible as shoulders in the spectra for both the nanorods and the bulk single crystal, will be discussed in more detail below.

Typical Raman spectra and PL spectra for C_{60} nanorods and bulk single crystals treated at 2 GPa, 700 K are shown in figure 3. The pentagonal pinch mode shifts from 1469 to 1448 cm^{-1} for both C_{60} nanorods and the bulk single-crystal sample, indicating that all samples have been transformed to the T polymer phase. As for the O phase, most of the Raman modes in polymeric nanorods are broader and weaker than those of the bulk single-crystal polymer. It has been reported that it is difficult to obtain bulk C_{60} samples with a pure T phase, and often there is a trace of R phase in bulk samples in previous studies [10]. A small peak at 1408 cm^{-1} was indeed observed on the shoulder of the peak at 1448 cm^{-1} in figure 3(a), indicating that a small amount of the R phase also co-exists with the T phase in our samples. Typical PL spectra for
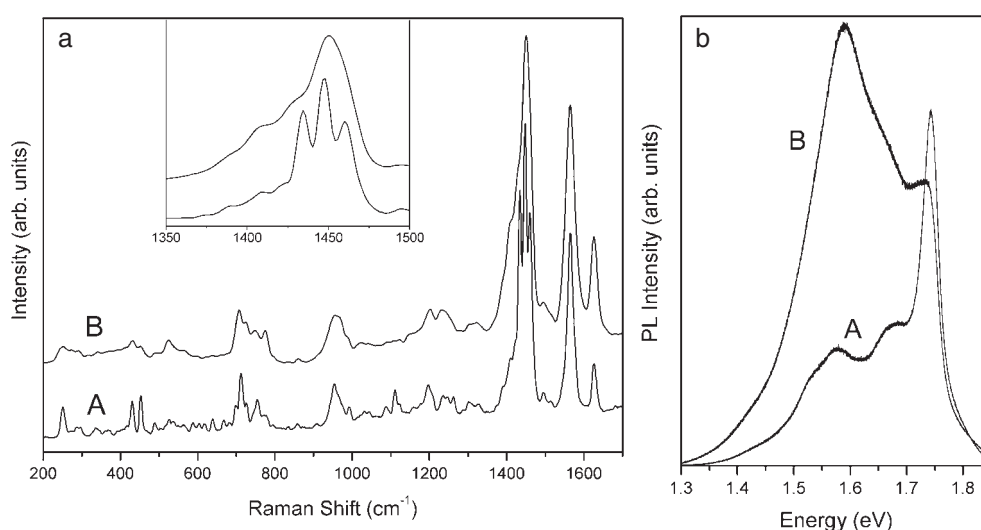
Figure 3. (a) Raman spectra and (b) PL spectra for C_{60} bulk single crystals (A) and C_{60} nanorods (B) treated at 2 GPa, 700 K (T phase).

the T phase in C_{60} nanorods and bulk single-crystal samples are shown in figure 3(b). The PL spectra of the nanorods have two main peaks at 1.58 and 1.74 eV, and the PL spectra of the bulk single crystals contain the same peaks plus an additional peak at 1.67 eV. In our previous study, the main peak for the T phase in C_{60} nanorods was at 1.588 eV [27]. Comparing with the T phase bulk single crystals, we consider that the 1.58 eV peak is characteristic for the PL of the T phase. Regarding the origin of the peak at 1.67 eV, which is clearly observed for the T phase of the bulk single crystals and shows up as a shoulder for the T phase of the nanorods, we may get information from the Raman data. It is noted that the Raman spectrum of the bulk single crystals is much sharper than that of the nanorods, and an obvious shoulder at 1458 cm^{-1} is observed in the $A_g(2)$ region, indicating that a small amount of the O phase co-exists in the bulk single-crystal sample. As mentioned above, 1.67 eV has been attributed to the O phase. We thus suggest that the observed peak at 1.67 eV is from the O phase. Other peaks, one at 1.74 eV which forms a shoulder for the nanorods and a dominant peak in the bulk single crystal, and one at 1.53 eV which forms an obvious shoulder for the bulk single crystal, will be discussed in more detail below.

The Raman and PL spectra for C_{60} nanorods and microrods treated at 4.5 GPa, 973 K are shown in figure 4. Here the pentagonal pinch mode shifts from 1469 to 1408 cm^{-1} for both the nanorods and the micrometer rod sample, indicating that both have been transformed to the R polymeric phase after treatment. The intensity of the 1408 cm^{-1} line for the micrometer C_{60} rod is higher than that for the nanorods. For both samples the PL spectra show a clear peak near 1.53 eV and a shoulder at 1.74 eV. We suggest that the 1.53 eV fluorescence band is attributed to the R phase, which is consistent with our previous study on nanorods, in which the 1.74 eV peak was shown to originate from surface defects [26]. The peak at 1.53 eV in the O and T phases discussed above thus indicates that there is a small amount of R phase in the T-phase samples. The peak at 1.74 eV in the O, T and R phases is generally attributed to surface defects, according to our previous study [26]. We thus find that the main fluorescence band shifts from 1.70 eV in the pristine sample to 1.66 eV in the O phase, to 1.58 eV in the T phase and to 1.53 eV in the R phase. The shift thus becomes stronger when the number of intermolecular
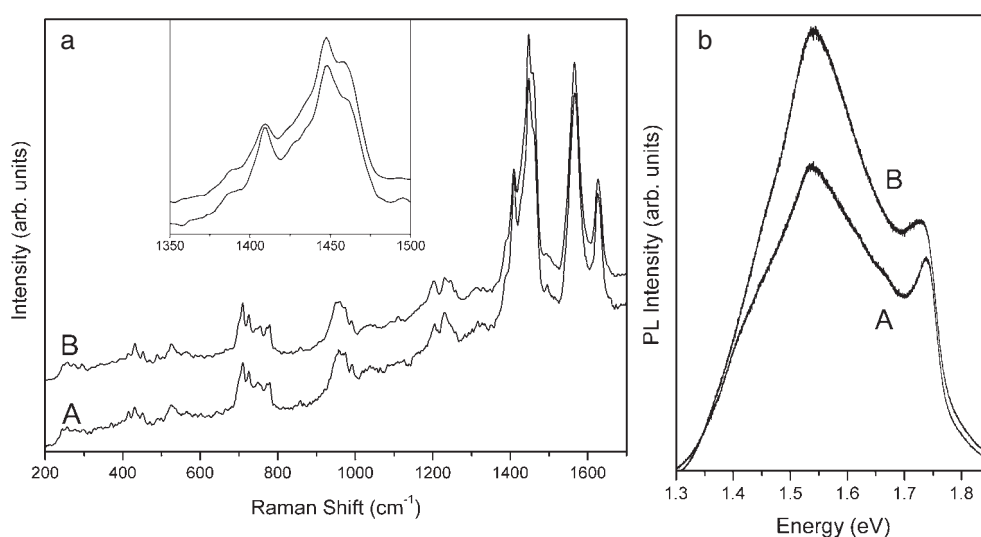
Figure 4. (a) Raman spectra and (b) PL spectra for C_{60} micrometer rod (A) and C_{60} nanorods (B) treated at 4.5 GPa, 973 K (R phase).

bonds per molecule increases. At the same time, the PL intensity from the nanorods decreases and the shift in the PL peak increases with an increasing number of bonds.

Both Raman and PL spectra of nanorods and of single-crystal C_{60} are, in general, noticeably different after polymerization. For example, the PL peak positions are slightly different and the PL intensity from C_{60} nanorods is higher than that from bulk single crystals. These differences may be explained by the domain structure of the various polymeric phases. In bulk samples, a nominal single crystal transformed into the O phase contains a number of differently oriented domains after polymerization. Each domain has one of 12 possible orientations relative to the original lattice because all (110) directions are equivalent for the O phase [10, 14]. Similar, basically random (disordered) domain structures must exist in bulk T and R samples. A polymeric nanorod sample probably has a different domain structure than a bulk single crystal because of its 'infinite' length and finite width and height. In fact, nanorods probably have polymer domains comparable in size with, or at least extending a significant fraction of, the width or thickness of the rod. In such a case the strain created in each domain during polymerization should be much smaller in the nanorod than in a truly bulk material. At the same time, the domain structure in the bulk single-crystal polymeric samples is probably more disordered than for the relatively well-ordered domains possible in polymeric nanorods. There might thus be structural differences both on the local (molecular) scale and the global (lattice) scale, giving a slightly different average shape and symmetry of the C_{60} molecules in a nanorod sample than in a bulk single crystal, and these differences should be reflected in the electron band structure and thus in the PL spectra.

Subtle differences are also observed between the Raman spectra of nanorods and bulk single crystals in the T phase, with some peaks diminished or decreased significantly. Most of the Raman modes in polymeric nanorods are much broader than those in bulk single crystals, for all polymeric phases, and the differences increase with the average number of intermolecular bonds formed, such that these phenomena are more obvious in the T phase than in the O phase. This broadening of the Raman peaks is probably mainly due simply to the small dimensions

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of the nanorods, with two dimensions in the range of a few hundred nanometers, while in the single crystal the domains are larger, giving more well-defined phonon frequencies and thus sharper peaks. The absence or weakness of some lines may also be due to domain effects similar to those discussed above for the PL.

We thus find differences in both electronic (PL) and lattice (Raman) properties between polymer samples produced from C_{60} nanorods and bulk single crystals, respectively, and we have shown that these differences can all be traced back to the very small dimensions of the nanorods compared to the bulk single crystals, and to the resulting differences in domain structures of the final materials.

4. Conclusions

In this paper, we report on a comparative study of pressure-induced polymerization of C_{60} nanorods and bulk single crystals in the same experiment under various pressures and temperatures. O, T and R phases of C_{60} nanorods and bulk single crystals have been obtained under high pressure and high temperature. The polymeric phases have been identified and studied by Raman and photoluminescence spectroscopy. There are slight differences in the Raman and photoluminescence spectra for the polymeric phases between the two types of samples, especially for the T phase. The shift of the main fluorescence band increases with the number of intermolecular bonds. In three samples of polymeric nanorods, the PL intensity decreases continuously as the degree of polymerization increases. From a comparison between the nanorods and bulk samples, we tentatively assigned some unclear photoluminescence peaks to various polymeric phases, such that a peak at 1.66 eV is from the O phase, 1.58 eV is the main peak in the T phase, and 1.53 eV is a characteristic feature of the R phase.

Acknowledgments

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