Diamond & Related Materials xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Raman identification of C_{70} monomers and dimers

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ARTICLE INFO

Article history:
Received 22 June 2016
Accepted 1 September 2016
Available online xxxx

Keywords:
Fullerenes
Metastable phases
Nanostructures
High pressure high temperature

ABSTRACT

Fullerenes easily polymerize under high pressure by forming covalent intermolecular bonds. For C_{60} this reaction is easily monitored by Raman scattering, but for C_{70} no simple method to determine its bonding state is known. In this work C_{70} has been heated over a wide range of temperatures at a pressure of 1.6 GPa and the treated material has been studied by Raman spectroscopy, using 830 nm laser excitation to avoid photo-induced polymerization. By comparing the present data with earlier results for pure dimers, zig-zag chain polymers and pressure treated powders, characteristic fingerprint peaks can be found for the C_{70} monomer and the C_{140} dimer. The molecular stretching mode near 88 cm^{-1} is a clear fingerprint for dimers while the strong A_1' peak near 455 cm^{-1} clearly shows the presence of monomers. Several other new peaks appear in pressure-treated material and the relative intensities of many peaks change in a systematic way, but it is not clear whether these changes indicate the presence of dimers or of small oligomers in general. Simple strategies for semi-quantitative structural analysis of pressure-treated C_{70} material by Raman spectroscopy are briefly discussed.

1. Introduction

Fullerene molecules in solid crystals easily form covalent bonds with their molecular neighbors when exposed to irradiation or to elevated temperatures at high pressure. The high pressure reactions of the most common fullerene, C_{60}, have been investigated in a large number of experiments reviewed, for example, in refs. [1–4]. In contrast, for the slightly larger molecule C_{70} only a relatively small number of studies have been carried out [1–3,5–6]. While C_{60} has 30 reactive double bonds, C_{70} has only ten, with five of these distributed radially around each pentagonal "polar cap". C_{70} is thus in practice much less reactive than C_{60} and the bonds formed are highly directional. At ambient conditions C_{70} usually forms a face centered cubic structure with freely rotating molecules. When pressure is applied the free rotation stops and the molecules line up with their poles in the original 111 direction of the lattice while retaining a uniaxial rotational motion. In this rhombohedral state the three-fold symmetry of the lattice is not compatible with the five-fold symmetry of the reactive bonds and it has long been believed that in this state only molecular dimers, but no long-range ordered polymers, can be formed. This assumption was recently challenged by the discovery of two long-range ordered polymeric structures formed above 7 GPa at elevated temperatures [5,6]. On the other hand, starting from the more unusual A-B stacked hexagonal close-packed structure, C_{70} can also form a long-range-ordered polymer, consisting of zig-zag molecular chains, near 2 GPa [7].

Fullerenes are interesting components for the synthesis of novel nanocarbon-based materials under mild pressure conditions. While graphene and carbon nanotubes are practically inert at low pressures, the fullerenes react easily and thus may act as a "glue" in the synthesis of such materials. Alternatively, fullerene molecules can be solvated in a matrix and if their positions and orientations are favorable, high pressure reactions can produce anisotropic or open structures with predictable structures and interesting and tunable properties. The fact that intermolecular bonding in C_{70} is strongly directional makes this molecule particularly suitable for such experiments and it is thus of some interest to investigate in detail its reaction properties under high pressure conditions.

In this work, the high pressure dimerization of C_{70} is studied up to 600 K at 1.6 GPa in an attempt to find a suitable method for semi-quantitative analysis of the bonding reaction under pressure. Recently, it was shown that the reaction diagram of C_{60} could be analyzed in a semi-quantitative way by Raman scattering, such that the relative amounts of monomers, dimers, one- and two-dimensional polymers and disordered oligomers could be deduced from the relative shift of the $A_g(2)$ "pentagonal-pinch" mode and the dimer and chain stretching modes [8]. For C_{70}, no such easy and convenient method is known and the present work should be seen primarily as an attempt to evaluate different ways to identify the relative amounts of monomers and dimers in pressure-treated material using near-infrared (NIR) Raman scattering.

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http://dx.doi.org/10.1016/j.diamond.2016.09.001
0925-9635/

2. Experimental details

A simple technique for accurately mapping reaction diagrams for high pressure reactions resulting in metastable phases was recently developed [9] and used to map the intermolecular bonding reaction in the fullerene C_{60} under pressures up to 2 GPa at temperatures up to 700 K [8]. The same basic technique was used here. In brief, the sample was deposited on a copper strip which was heated at one end. The temperature was measured at six points along the strip by putting thin, calibrated Constantan wires in contact with the copper and pressure was applied in a large piston-cylinder vessel, using Teflon and a small amount of talc powder as quasi-hydrostatic pressure-transmitting media. For the present experiment, 99.5% pure C_{70} obtained from BuckyUSA, Houston, TX, was dried for more than 24 h at 200 °C under dynamic vacuum (created by a turbomolecular pump) and the dried material was deposited on the copper strip in a glove-box under Ar gas with water and oxygen levels below 1 ppm. The pressure in the cell was increased to 1.6 GPa after which the hot end temperature was increased at an approximate rate of 20 K/min and held at the maximum temperature for 2 h. The power was then switched off, resulting in a rapid temperature quench to near room temperature, before the pressure was slowly released to atmospheric pressure.

The pressure cell was opened and the sample removed under red darkroom light to avoid additional photopolymerization. During the pressure treatment the sample was compressed to form thin solid plates. The surfaces facing the Cu strip were analyzed using Raman scattering, using a NIR laser (wavelength 830 nm) to avoid photopolymerization. Treatment temperatures were deduced from positions using the known temperatures at the thermocouple positions. The Raman spectra obtained were analyzed in detail using PeakFit™ software [10].

3. Experimental results and discussion

Fig. 1 shows the Raman spectrum of dried, pristine C_{70} when excited by an 830 nm NIR laser. Because the detector used suffers from a gradually decreasing sensitivity for Raman shifts exceeding about 500 cm^{-1} the spectrum shown has been corrected using an exponential decay function. A comparison between Fig. 1 and the Raman spectra of similar materials given by Lebedkin et al. [11] and Soldatov et al. [7] using 1064 nm excitation shows that the three spectra are in excellent agreement regarding both frequency shifts and relative amplitudes. For all stable fullerenes, more than one isotope of carbon is present in most molecules, breaking the molecular symmetry [12]. Although C_{70} formally has only 53 Raman allowed lines, a careful study will thus show many more peaks in the spectrum, many of these quite weak but clearly rising above the noise.

The dimer C_{140} has previously been synthesized in several experiments. Lebedkin et al. [11] produced C_{140} in high yield at a pressure of 1 GPa at a temperature near 473 K and purified the dimer by liquid chromatography. The zig-zag chain polymer of C_{70} was later produced from hexagonal close-packed C_{70} at 2 GPa and 573 K by Soldatov et al. [7]. Good Raman spectra, measured using 1064 nm NIR excitation, are available for both materials and the spectra obtained in this work were analyzed and compared to the spectra of both these phases.

In the present investigation the C_{70} sample was treated at 1.6 GPa, intermediate between the pressures used by Soldatov et al. [7] and Lebedkin et al. [11], and the total temperature range studied was about 360 to 600 K. The reaction time at elevated temperature was chosen as 2 h to ensure that the dimerization reaction had been completed. For the present sample, a total of 43 Raman spectra were measured using NIR laser excitation and Fig. 2 shows eight of these. In the range from 370 to about 500 K there was a clear evolution of the spectra with increasing treatment temperature and spectra are shown for seven different treatment temperatures in this range. Above 500 K little further change was observed, and only the final spectrum obtained for material treated at close to 600 K is shown. Most spectra were measured over the range 50–1600 cm^{-1}. However, with increasing treatment temperature the quality of the spectra deteriorated due to an increasing background level. Because the sensitivity of the detector also decreased at high wavenumbers the spectra shown have been limited to the range below 500 cm^{-1}. This range includes most of the Raman lines useful for the identification of dimers and the expansion of the scale also facilitates the discussion of the spectra. Note that the intensities of the spectra shown have been approximately normalized using the product of the laser intensity used and the exposure time, and the spectra have been shifted vertically by arbitrary amounts to allow easy comparison. No background correction has been applied. The peaks were analyzed by fitting Voigt functions to the data, and the areas of the fitted peaks will be referred to in the following as the "intensities" of the peaks.

A comparison between Figs. 1 and 2 shows that material treated at 370 K has a Raman spectrum essentially identical to that of the pristine material, but with increasing treatment temperature the intensities of the different lines change and several new lines appear. For most of the Raman lines observed for pristine C_{70} there is a slow decrease in intensity with increasing treatment temperature.

The most important of the new modes observed is the low-frequency dimer stretching mode at 88 cm^{-1}. For individual C_{70} molecules no Raman modes exist in this frequency range and this mode can thus be positively identified and used as a fingerprint for the existence of dimers in the sample. The same mode was observed at 89 cm^{-1} by Lebedkin et al. [11], in excellent agreement with the present result. This mode is not observed in pristine C_{70} and for material treated at 370 K it is too weak to be observed on the scale of the figure. However, as shown in Fig. 3 the intensity grows rapidly with increasing treatment temperature until it saturates near 500 K. Above this temperature the intensity appears to be approximately constant, or even to decrease slightly with increasing treatment temperature. Lebedkin et al. also observe some weak, related modes between 118 and 130 cm^{-1}. However, no such modes could be identified in the present study although some spectra showed a low, broad "hump" structure centered on 124 cm^{-1}. For the zig-zag chain polymer the stretching mode was identified at 105 cm^{-1} with a weaker

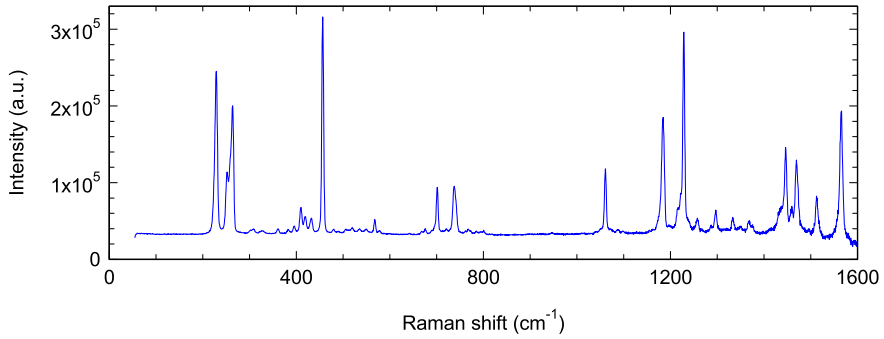

Fig. 1. Raman spectrum of pristine C_{70} before pressure treatment. The intensities have been approximately corrected for the drop in detector sensitivity with increasing Raman shift.

Please cite this article as: B. Sundqvist, Raman identification of C70 monomers and dimers, Diamond Relat. Mater. (2016), http://dx.doi.org/10.1016/j.diamond.2016.09.001