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Thermal stability of solid C_{60}

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We have used differential scanning calorimetry, optical microscopy, and x-ray diffraction to study the thermal stability of pristine C_{60} in the solid state. To minimize contamination and/or reaction of the sample with the container, sublimed single crystals and powder derived from resublimed C_{60} material were heated in hermetically sealed Au pans. Crystals heated at 1260 K for more than 10 min decomposed into amorphous carbon without losing their faceted morphology. [S0163-1829(97)02702-1]

I. INTRODUCTION

Much of the recent interest in C_{60}, buckminsterfullerene, can be attributed to the nearly spherical molecular architecture exhibited by this caged carbon compound, an architecture which profoundly influences the solid-state structures and dynamics of these molecules.[1,2] The existence and properties of a stable liquid phase of C_{60} have been the subject of numerous theoretical studies.[3–8] There is considerable theoretical disagreement about whether a triple-point and high-temperature liquid-vapor coexistence are to be expected in C_{60}, and on the value of the putative triple-point temperature. Even if precise calculations indicate the existence of a true C_{60} liquid phase, it may be experimentally inaccessible if the molecules themselves decompose below the triple-point temperature. Hence, a thorough understanding of the thermal stability of solid C_{60} is imperative if one ultimately wishes to characterize the high-temperature regime of the C_{60} phase diagram.

Molecular-dynamics simulations[9,10] have predicted gas-phase decomposition of C_{60} near 5000 K, possibly preceded by ''melting'' of the individual molecules. There have been several experimental studies of the thermal decomposition of C_{60} both in the gas phase[11–14] and in the solid state,[15,16] and even the gas-phase experiments have shown decomposition at temperatures well below those predicted theoretically. Sundar *et al.*[15] used x-ray powder diffraction (XRPD) along with uv-visible absorption spectroscopy and resistivity experiments in order to show that solid C_{60} begins to decompose into amorphous carbon when heated for 24 h at temperatures in excess of 973 K. In these thermal studies, C_{60} powder pellets of greater than 99% purity were heated for 24 h in evacuated quartz ampoules. Although x-ray patterns of samples heated to 973 and 1073 K exhibited a few broad Bragg reflections superimposed on an amorphous background, the x-ray pattern of a sample heated to 1173 K revealed only diffuse features characteristic of amorphous carbon. Leifer, Goodwin, Anderson, and Anderson (LGAA) quantified these decomposition kinetics by heating a fullerene mix (85% C_{60}, 15% C_{70}) sealed in evacuated quartz ampoules to several temperatures ranging from 873 to 1273 K for durations of 5 min to 6 h.[16] Under the assumption of unimolecular decay, LGAA determined an activation energy of 266 ± 9 kJ/mol for the thermal decomposition of C_{60}, significantly lower than prior estimates. Moreover, those samples heated to temperatures greater than 1273 K were insoluble in toluene and displayed no Bragg peaks, thus indicating that the samples had decomposed into amorphous carbon. Surprisingly, these samples still retained their external morphologies.

We have extended the work of LGAA by using pure C_{60} rather than a fullerene mix and by using gold pans rather than quartz tubes to contain the sample. We thus attempted to ensure that both the C_{60} sample and the heating vessel were free of any fullerene and nonfullerene impurities which could potentially nucleate premature decomposition. The presence of C_{70} in the sample complicates the story, both because the kinetics of C_{70} decomposition may not be the same of those of C_{60}, and because C_{70} molecules may act as nucleation sites of molecular or crystalline disruption in the C_{60} lattice. Therefore, we used samples consisting of either high-quality sublimed single crystals of C_{60} or powders derived from resublimed C_{60} material in order to minimize both higher-fullerene and solvent impurities. In addition, hermetically sealed gold pans were adopted as heating vessels to eliminate the possibility of the fullerene material reacting with O_2 from its quartz container at the elevated temperatures examined in these studies. Differential scanning calorimetry (DSC) was used to determine the purity and integrity of high-quality pristine C_{60} samples after various thermal treatments by monitoring the enthalpy change associated with the orientational ordering transition at $\sim$260 K.[17]

II. EXPERIMENTAL PROCEDURES

Three samples were studied. The first two were sublimed single crystals of C_{60}, and the third was a C_{60} powder.

Samples 1 and 2 had masses of 11.2 and 4.1 mg, respectively, each sample consisting of several small (volume < 2 mm^3) single crystals. Sample 3 consisted of a powder obtained by mortaring resublimed C_{60} material, thus allowing for x-ray powder diffraction (XRPD) both before and after heat treatment. The mortaring of the C_{60} was performed under an inert argon atmosphere to minimize contamination by impurities such as O_2. 10.2 mg of this powder were subjected to the heat treatments described below, and the remaining powder was used for an XRPD study of the material before heat treatment. In all cases, the samples were loaded under an inert argon atmosphere into hermetically sealed gold DSC pans of greater than 99.95% purity manufactured by TA Instruments.

For the XRPD studies, the C_{60} powder was transferred into 0.5 mm glass capillaries which were then sealed under vacuum. An incident beam of wavelength 1.5406 Å was collimated by a Gr(002) monochromator, and the diffracted beam was measured using an INEL position-sensitive detector; each diffraction profile was collected during 3600 s of detector live time. Single-crystal x-ray diffraction (XRD) measurements used an incident beam of wavelength 0.7107 Å collimated by a Gr(004) monochromator. The diffracted beam was collimated by Soller slits and detected with a NaI scintillation counter.

In order to monitor the decomposition of C_{60} as a function of successive heat treatments in a nearly *in situ* fashion, sample integrity was studied via DSC using a TA Instruments DSC 2920. The sample remained in the same hermetically sealed container at all times, thus minimizing handling and contamination. We performed an initial DSC scan on each sample prior to heat treatment in order to establish a baseline enthalpy change and onset temperature for the orientational ordering transition. After placing the sample into a Seiko Instruments TG/DTA 320 under a flow of high-purity argon, the sample temperature was then ramped at 20 K/min from room temperature to the elevated temperature of interest, and the sample was held at this annealing temperature for a specified time (usually 10 min). Upon completion of the anneal, the sample was allowed to cool naturally to room temperature before another DSC measurement was performed.

Any significant decreases in both the onset temperature and the enthalpy change of the endotherm associated with the sample's ordering transition were attributed to the decomposition of the crystalline C_{60} material. It is possible that the decomposition mechanism is such that large regions of the sample decompose completely while others remain intact. In this case, the integrated enthalpy change through the transition should be directly proportional to the amount of remaining crystalline C_{60}. Alternatively, individual molecules destroyed by the heat treatment may permeate the sample uniformly, functioning as point defects. In this case, the enthalpy change would most likely not be linearly proportional to the number of intact C_{60} molecules, although one would expect a monotonic relationship. In our measurements, the crystallinity of the sample was independently monitored via Bragg diffraction, and the existence of C_{60} molecules was tested via solubility in toluene. Since our samples failed to exhibit either strong Bragg reflections or solubility in toluene after their endotherms had disappeared, the decomposition mechanism appears to have destroyed both the material's crystalline order and the C_{60} molecules themselves, suggesting that the enthalpy change at the transition provides at least a qualitative indication of the amount of remaining crystalline C_{60}. Our procedure therefore was to perform multiple cycles of high-temperature annealing followed by calorimetry through the $\sim$260 K ordering transition.

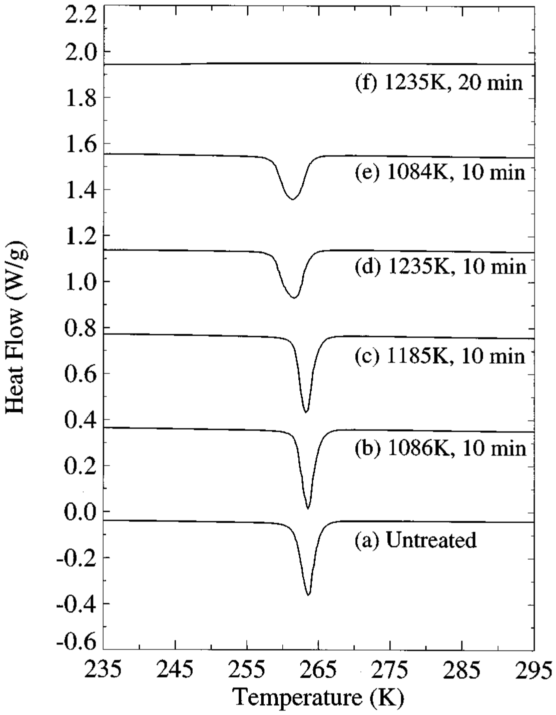

FIG. 1. Differential scanning calorimetry data collected upon heating for sample 1, the first of two single-crystal C_{60} samples studied. (a) shows the ordering transition endotherm exhibited by the material prior to heat treatment, while (b)–(f) show the endotherm after sequential anneals. The temperature and time of anneal are given for each scan, and the curves are offset for clarity. Significant sample decomposition was observed for annealing temperatures of 1235 K and above, with this decomposition manifesting itself in a lowering of the ordering transition's onset temperature and a decrease in the enthalpy change associated with the endotherm. Values of the onset temperature and enthalpy change for each scan are presented in Table I.

III. RESULTS

For sample 1 (single crystals), a preliminary DSC run indicated an enthalpy change of 11.2 J/g and an onset temperature of 261.81 K, both consistent with the values expected for high-purity single crystals. This baseline scan on the first sample as well as scans obtained after various heat treatments at temperatures ranging from 1086 to 1235 K are presented in Fig. 1; our results for this sample are summarized in Table I. Relatively little change in the ordering transition's endotherm was observed after thermal treatments at 1086 and 1185 K. After 10 min at 1235 K, the sample had decomposed significantly, as manifested in both the lowering of the onset temperature to 258.70 K and the 14.5% reduc-

TABLE I. Summary of phase transition onset temperatures and associated enthalpy changes obtained from DSC data for sample 1 after various thermal treatments. Results are listed in the order in which the anneals were performed.

T_{anneal} (K)	t_{anneal} (min)	T_{onset} (K)	ΔH (J/g)
Untreated		261.81 ± 0.02	11.2 ± 0.4
1086	10	261.91 ± 0.02	10.8 ± 0.4
1185	10	261.80 ± 0.02	10.3 ± 0.4
1235	10	258.70 ± 0.02	9.6 ± 0.4
1084	10	258.68 ± 0.02	9.4 ± 0.4
1235	20	213 ± 2	1.2 ± 0.2

tion of the enthalpy change to a value of 9.6 J/g. Annealing the sample at a lower temperature of 1084 K failed to improve the integrity and crystallinity of the sample. After 20 additional min at 1235 K, the onset temperature was lowered to 213 K and the associated enthalpy change was reduced to 1.2 J/g. If, as discussed in the previous section, we associate the enthalpy change with the quantity of remaining crystalline C_{60}, this is consistent with approximately 11% of the sample remaining as crystalline C_{60}. At this point, the remaining sample was placed in toluene, which is known to be a good solvent for C_{60}. The majority of the material did not dissolve, but the appearance of a faint purple tint indicated that some did, consistent with the hypothesis that a small fraction of the sample remained as unmodified C_{60}. The integrity of our measurements on sample 1 was somewhat compromised by the subsequent discovery of small translucent lumps of material among the decomposed C_{60} crystals, provisionally identified as arising from small glass shards inadvertently loaded with the sample.

Sample 2, also consisting of single crystallites, was prepared in a similar manner. An initial enthalpy change of 9.0 J/g, a measured onset temperature of ~255.52 K, and a splitting in the major endotherm indicated that this sample was not quite as pure and defect free as sample 1. In addition, a very small endotherm with an onset temperature of approximately 280 K indicated the presence of a small amount of $C_{60}O$ in the sample.[18] The sample was heated for 10 min at 1034, 1137, 1187, and 1237 K with no noticeable degradation. After 10 min at 1262 K, the enthalpy change associated with the endotherm decreased from 8.9 to 7.3 J/g, this decrease being accompanied by a broadening of the endotherm. After an additional 10 min at 1261 K, the major endotherm disappeared entirely. At this point, material from this sample was insoluble in toluene, consistent with the hypothesis that all of the crystalline C_{60} had decomposed as a result of the heat treatment.

Measurements on sample 3, the resublimed C_{60} powder, yielded results similar to those obtained from the single-crystal samples; these results are presented in Fig. 2 and Table II. Before heat treatment, the endotherm had an enthalpy change of approximately 8.1 J/g, with an onset temperature of 257.31 K. The relatively broad precursor below the endotherm can most likely be attributed to the presence of stacking faults in the sample resulting from the mortaring procedure.[19] Annealing at 883 K for 4 h had no noticeable effect on the endotherm. Minor degradation of the endotherm was observed after heat treatment at both 1212 and 1221 K. After 10 min at 1232 K, the enthalpy change through the transition was reduced to 4.5 J/g and the onset temperature was dramatically lowered to 239.3 K. This enthalpy change was further reduced to 1.3 J/g, approximately 16% of its original value, after 10 min at 1240 K. The DSC scan performed on the sample after a final heat treatment at 1250 K

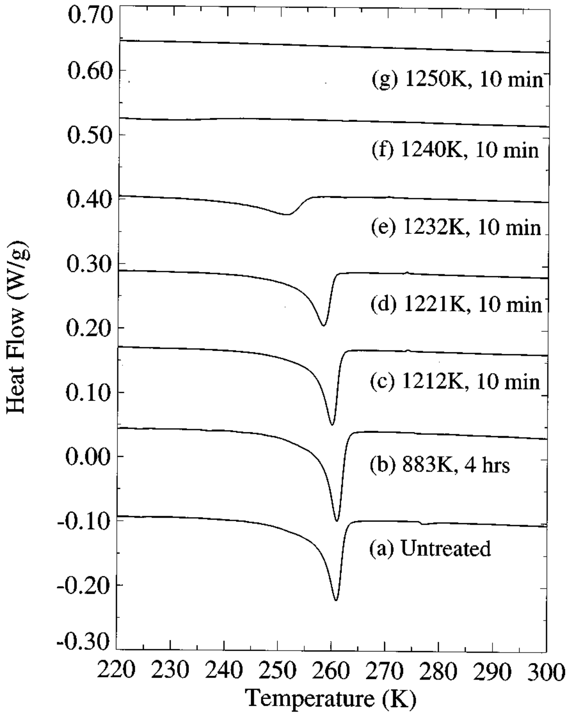

FIG. 2. Differential scanning calorimetry data collected upon heating for sample 3, a powder derived from resublimed C_{60} material. (a) shows the ordering transition endotherm exhibited by the material prior to heat treatment, while (b)–(g) show the endotherm after sequential anneals. The temperature and time of anneal are given for each scan, and the curves are offset for clarity. The broad precursor to the untreated sample's endotherm, shown in (a), was attributed to stacking faults introduced into the material as a result of mortaring. Significant sample decomposition was observed for annealing temperatures of 1232 K and above. Values of the onset temperature and enthalpy change for each scan are presented in Table II.

TABLE II. Summary of phase transition onset temperatures and associated enthalpy changes obtained from DSC data for sample 3 after various thermal treatments. Results are listed in the order in which the anneals were performed.

T_{anneal} (K)	t_{anneal}	T_{onset} (K)	ΔH (J/g)
Untreated		257.31 ± 0.02	8.1 ± 0.4
883	4 h	257.70 ± 0.03	8.0 ± 0.4
1212	10 min	256.51 ± 0.01	7.2 ± 0.3
1221	10 min	253.78 ± 0.03	6.3 ± 0.5
1232	10 min	239.3 ± 0.4	4.5 ± 0.6
1240	10 min	207 ± 2	1.3 ± 0.2
1250	10 min	214 ± 2	0.14 ± 0.09

FIG. 3. A single grain of C_{60} from sample 2 after annealing at 1261 K. Single-crystal XRD on this grain revealed only extremely weak 111 and 200 reflections superimposed upon a significant amount of diffuse scattering, and subsequent XRPD resulted in an entirely amorphous spectrum. However, the slightly pitted surface of the thermally treated grain retained its original faceted morphology even after the decomposition of crystalline C_{60}, suggesting that the decomposition took place in the solid state.

revealed only an extremely weak endotherm. Given the error bars of ±0.09 J/g associated with the endotherm's integrated enthalpy change of 0.14 J/g, this result is consistent with the complete decomposition of the sample.

In all of our work on both single crystals and powders, significant decomposition of the C_{60} samples began when $T \geqslant 1232$ K, and complete decomposition on the 10-min time scale took place in the 1250–1262 K temperature range. These results are qualitatively consistent with LGAA's observation that fullerene samples heated to temperatures in excess of 1273 K fully decomposed into amorphous carbon.[16]

Both sample 1 and sample 2 were still faceted after heat treatment (Fig. 3), although the faces of the samples were somewhat pitted. This indicates that, although the C_{60} vapor was certainly quite high at the treatment temperatures, most of the sample remained in the solid state throughout the annealing process, and that C_{60} decomposition took place in the solid state. Single-crystal XRD performed on a crystal from sample 2 revealed the presence of extremely weak 111 and 200 reflections as well as a significant amount of diffuse scattering. An entirely amorphous pattern, however, was obtained from XRPD upon crushing this same crystal into powder, thus implying that, at most, a very small fraction of the thermally treated sample was crystalline C_{60}. XRPD patterns from sample 3, the powdered C_{60} sample, both before heat treatment and after heat treatment up to 1250 K are shown in Fig. 4. The rather large stacking-fault foot below the crystalline 111 reflection in the XRPD spectrum collected before heat treatment [Fig. 4(a)] resulted from the mortaring of the sample, and is consistent with the broad precursor observed below the main endotherm in the sample's preliminary DSC scan.[19] The XRPD profile collected after heat treatment at 1250 K reveals a broad amorphous pattern, although one very weak reflection appears to exist at $Q = 0.752$ Å^{-1} [Fig. 4(b)]. This feature is at too small an angle to be identified as the 111 reflection from pristine C_{60} ($Q = 0.772$ Å^{-1}), but may correspond to the 111 reflection after lattice dilation resulting from heat treatment, an effect that Sundar *et al.* observed in their studies of C_{60} pellets.[15]

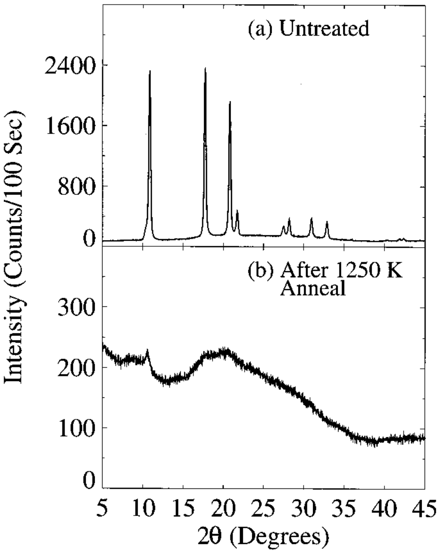

FIG. 4. X-ray powder-diffraction patterns for sample 3, a C_{60} powder, collected (a) prior to heat treatment and (b) after annealing at 1250 K. Both patterns were counted for 3600 s of detector live time. Note the change in vertical scale between the top and bottom curves. Pattern (b) demonstrates the primarily amorphous nature of the treated material, although the weak reflection at $Q = 0.752$ Å^{-1} may correspond to the 111 reflection in a dilated C_{60} lattice, indicating that a small amount of crystalline C_{60} survived the annealing procedure.

IV. CONCLUSIONS

We have examined the thermal stability of high-purity C_{60} in the solid state using DSC and XRPD. On the time scales used in these experiments, ''total'' decomposition of the sample was observed to occur at temperatures between 1250 and 1262 K, manifesting itself through the disappearance of the characteristic C_{60} ordering transition and its associated endotherm. Qualitatively, our results are similar to those obtained by LGAA for fullerene mixes, thus ruling out the possibility that premature decomposition may have been induced in the latter experiment as a result of C_{70} or O_2 impurities. In light of the low activation energy suggested by these studies for the solid-state decomposition of pristine C_{60}, it is improbable that a liquid phase of C_{60} will ever be observed since the solid will necessarily decompose at temperatures well below the liquid regime predicted[8] to exist between 1600 and 1920 K.

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