Rapid Synthesis of Alkali-Metal Fullerides Using a Microwave-Induced Argon Plasma

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The rapid synthesis of alkali metal fullerides using a microwave-induced argon plasma (MIAP) is reported. Reaction times are of the order of seconds using a MIAP, whereas conventional synthesis requires times of the order of several days. Potassium, rubidium, and cesium fullerides are more readily synthesized by this technique than sodium fullerides. Investigation of sodium fulleride synthesis via both conventional and microwave routes, combined with ^{13}C MAS NMR spectroscopy and powder X-ray Rietveld analysis, gives an improved understanding of the sodium−C_{60} phase diagram.

Introduction

Since the discovery of superconductivity[1] in K_3C_{60}, alkali-metal fullerides have been the subject of much attention. Synthesis is typically achieved by direct combination of stoichiometric quantities of alkali metal and C_{60} or by dilution of the saturated alkali metal A_6C_{60} phase (A = K, Rb, and Cs) with C_{60}.[2] A number of solution routes for the synthesis of K_3C_{60} and Rb_3C_{60} have also been developed.[3−6] Sodium C_{60} intercalate phases extend beyond the composition Na_6C_{60}, as sodium clusters can be accommodated on the octahedral site of the fcc C_{60} array. A composition $Na_{9.8}C_{60}$ has been structurally characterized.[7] Sodium C_{60} intercalates have been synthesized using a number of sodium precursors such as sodium metal,[7,8] Na_5Hg_2, NaH, and $NaBH_4$[8] or by reaction of Na_9C_{60} with C_{60}.[9] No binary lithium C_{60} intercalates have to date been structurally characterized.

As is common with solid-state synthesis, reaction times are long, on the order of several days to weeks. Reaction temperatures of less than 700 °C are generally required to avoid thermal decomposition of the C_{60} molecule, especially as the antibonding t_{1u} orbitals are populated in the fulleride products. The temperature is typically increased to 4−500 °C over a period of several days and held there for 1−2 weeks, with several intermittent regrindings required to produce single-phase products.

There are two processes that cause the time required for synthesis of alkali-metal fullerides to be on the order of days; mass transport of alkali-metal atoms through the vapor phase to the surface of the C_{60} solid and diffusion of alkali-metal cations throughout the bulk of a C_{60} particle. Solution methods circumvent mass transport and diffusion of the alkali metal by mixing the constituent components on the molecular level in a precursor. As the solvent required is generally a coordinating, polar one such as ammonia or THF, the precursor will contain solvated cations. To remove coordinating or occluded solvent and prepare materials of crystallinity comparable to those produced by solid-state synthesis, annealing at temperatures comparable to those required for conventional thermal synthesis is then needed.

Microwave techniques have been used for synthesis in reaction media ranging from the gas phase and homogeneous solution to the solid state.[10] The vast majority of these reactions are effectively superheated via dielectric loss. This requires that at least one of the reactants absorbs microwave radiation at the applied frequency (2.45 GHz in this case). In the solid state, if none of the reaction components absorb microwave radiation at the applied frequency, then an absorber such as graphite can be added to mediate energy transfer.[10] Separation of the mediator from the reaction product is then required.

Although dielectric heating is the most familiar action of microwaves on a chemical reaction mixture, microwaves can also induce plasmas in gases. Microwave induced plasmas have been investigated for over 45 years.[11] They have been applied to thin-film technology in the form of microwave plasma chemical vapor

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deposition[12−15] and in the generation of species in situ for deposition, e.g., arsine from metallic arsenic and dihydrogen.[13] Microwave plasma-induced sintering[16−19] has also been demonstrated for ceramics where temperatures in excess of 1600 °C have been readily achieved using a range of gases at various pressures. Diatomics produce higher temperatures than monatomic gases due to release of the association enthalpy on the solid surface as species dissociated in the gas phase recombine there. The decomposition of cobalt carbonyl in a series of zeolites has also been reported to yield cobalt clusters within the zeolitic cavities.[20]

We recently described the preparation of K_3C_{60} using a microwave-induced argon plasma (MIAP).[21] In this paper we describe in detail the rapid synthesis of a variety of alkali-metal fullerides using a MIAP and compare the resulting fullerides with those prepared using conventional thermal routes. We demonstrate that a MIAP can be generated in a common household microwave oven and used to vaporize alkali metals and produce rapid diffusion of alkali-metal cations in solid C_{60}. Synthesis of the superconducting fulleride phases is achieved both by direct reaction of the alkali metal and C_{60} followed by composition adjustment and annealing and by plasma-induced reaction of C_{60} with A_6C_{60} fullerides. The observation of rapid synthesis induced by the argon plasma is novel and may find wider application in solid-state synthesis. We also report new information on the Na_xC_{60} phase diagram resulting from combined ^{13}C magic angle spinning (MAS) NMR spectroscopy and powder X-ray diffraction characterization of solids prepared by microwave and thermal routes.

Experimental Section

Materials. Synthesis was performed in a Hinari Lifestyle 1000 W microwave oven operating at a frequency of 2.45 GHz, modified to incorporate a variable-power unit. Argon for the microwave-induced plasma was used as provided by BOC Ltd. Sintered alumina (Andemann and Ryder) and zirconia (Goodfellow) for the construction of the ceramic furnaces were fashioned using a diamond drill bit. Sodium, potassium, rubidium, and cesium metals were purchased from Aldrich Chemicals and cut to suitably sized pieces using a clean scalpel blade (sodium, potassium, and rubidium) or transferred using a dry Pasteur pipet (cesium) in a helium-filled drybox. Fullerene-rich soot was prepared using carbon are vaporization[22] and separation of C_{60} was performed by column chromatography using activated neutral alumina and hexane as purchased from Aldrich Chemicals. C_{60} powder was obtained by sublimation of material purified by column chromatography under a dynamic vacuum of 10^{-3} Torr at 500 °C.

Powder X-ray Diffraction. Samples were contained in 0.5 mm diameter capillaries sealed under helium. Data were collected in transmission geometry on a Siemens D5000 instrument with a 6° linear position-sensitive detector and Cu $K\alpha_1$ radiation from a germanium (111) incident beam monochromator. Rietveld refinement was performed on data collected in 0.02° steps using the GSAS software;[23] the background was fitted using a 10-term power series expansion and the peak shape described with a pseudo-Voigt function.

Solid-State NMR. Samples were contained in a KEL-F insert within a 7 mm zirconia rotor and spun at ca. 3 kHz. ^{13}C MAS NMR spectra were recorded at 50.32 MHz on a Brucker MSL200 spectrometer using an external reference on adamantane. Integration was performed by the cut-and-weigh method or electronically.

Magnetic Measurements. A 2.6 mg sample of K_3C_{60} prepared using microwave techniques was flame sealed in a 2 mm quartz capillary under helium. Dc static susceptibility measurements were performed using a Cryogenic Consultants S600C SQUID magnetometer. Zero field (ZFC) and field (FC) cooled magnetization measurements were made from 6 to 40 K in a 10 Oe field.

Sample Preparation. All samples were manipulated in a helium-filled MBraun Labmaster drybox, with the helium purified over molecular sieves and a hot copper catalyst. Argon was introduced using standard Schlenk techniques with dual argon and vacuum manifolds. Pressures of less than 10^{-3} Torr were obtained using a turbomolecular pump. Samples for comparison with those prepared using microwave techniques were prepared by conventional thermal methods described in the literature.[2]

Conventional Synthesis. Sample sizes of between 30 and 50 mg were prepared. A_xC_{60} phases ($x = 1$ for Rb and Cs; $x = 3$ for K and Rb; $x = 4$ for K, Rb, and Cs) were prepared from the saturated $A_{6+x}C_{60}$ phase and an appropriate quantity of C_{60}. Samples were heated in Pyrex tubes sealed under 10^{-5} mbar at 350 °C for 7 days with an intermediate grinding. Sodium C_{60} intercalates were prepared from stoichiometric quantities of freshly cut sodium metal and C_{60} powder. Reactions were performed in a stainless steel tube sealed within a silica tube under 10^{-5} mbar and heated from room temperature to 400 °C over 3 days and annealed at 450 °C for a further 7 days with two intermediate grindings. One sodium fulleride sample (of composition Na_1C_{60}) was sealed in a helium-filled tantalum tube by dc argon arc welding and subsequently sealed under 10^{-5} mbar in a silica tube. The sample sealed in tantalum was heated at 450 °C over 4 days , 550 °C for 4 days, and 600 °C for a further 3 days. All samples were checked for mass balance. Phase purity of all materials was confirmed by powder X-ray diffraction and ^{13}C MASNMR spectroscopy.

Microwave Synthesis. We found that alkali metals can easily be vaporized by a MIAP using the apparatus shown in Figure 1. Reaction vessels were supported on firebricks to reduce thermal contact with the cavity walls. The alkali metal (typically present in a 10-fold molar excess) is placed in an alumina crucible, which was used to restrict violent vaporization of the metal and subsequent reduction of the silica. The C_{60} powder is physically separate from the alkali metal in the reaction vessel. The vessel was placed under argon at 10^{-5} mbar. The plasma was initiated by gradually increasing the power of the applied microwave radiation up to the maximum output available (estimated at 400 W from a measurement of the temperature increase in a known volume of water). The plasma initiates within 5 s. The power is then ramped to its maximum value over a further 5 s, and the C_{60} is then exposed to the plasma at full power for 20 s. The focus of the plasma was controlled by positioning the reaction vessel at an antinode or a node in the oven cavity. The position of the apparatus is adjusted so that the C_{60} is located in a diffuse region at the

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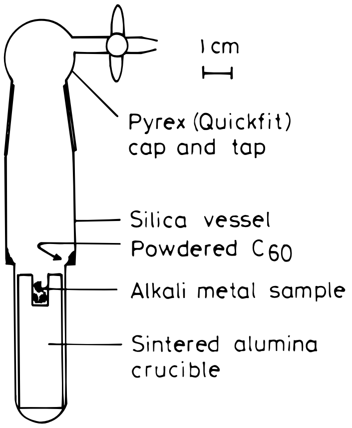

Figure 1. Apparatus used for synthesis of alkali-metal fullerides using microwave radiation.

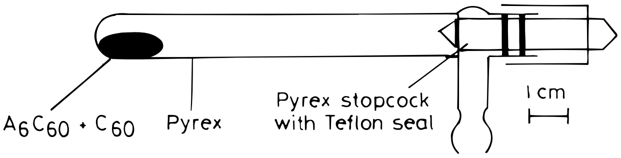

Figure 2. Apparatus for the annealing of a $K_yC_{60} + C_{60}$ or $A_6C_{60} + C_{60}$ alkali-metal fulleride reaction mixture.

edge of the plasma. The composition of the resulting K_yC_{60} phase assemblage was determined via ^{13}C MAS NMR by integration of the relevant peaks corresponding to the known K_xC_{60} phases ($x = 3$, 4, and 6).

An appropriate quantity of C_{60} powder was then added to the phase assemblage to give the desired composition, and after grinding in an agate mortar, the reaction mixture was exposed to a MIAP in the apparatus shown in Figure 2 (it is important to ensure that the PTFE seal is not exposed to the plasma). In a typical reaction, a 50 mg sample was sealed under 10^{-1} mbar of argon (a convenient pressure to achieve on a Schlenk line, but not critical to the success of this step which will proceed equally well at lower pressures) and exposed to a MIAP at the full power available for two periods of 5 s. Exposing the sample to 5 s pulses of the MIAP avoided localized heating by the plasma and possible tube failure.

Reaction between C_{60} and the saturated A_6C_{60} phases (A = K, Rb, Cs) prepared by conventional synthesis was carried out by grinding the materials together and annealing in a MIAP under 10^{-1} mbar of argon at the full available power for 2 × 5 s. This dilution method was also used to investigate the preparation of Na_1C_{60} and Na_3C_{60} from Na_2C_{60} and Na_6C_{60}, respectively.

Results

An argon plasma is readily generated in a microwave oven, affording a pink glow in the vessel and causing a rapid rise in temperature, depending on the power applied. Powers of a few tens of watts are needed to induce plasma formation, depending on the pressure of argon and the geometry of the vessel.[24] In the synthesis of alkali-metal fullerides, the MIAP accelerates both mass transport of alkali metal to the C_{60} surface and the second step of diffusion of the alkali-metal cation throughout the C_{60} particle. In the first step of the microwave synthesis, the vessel is placed under an argon pressure of 10^{-5} mbar to assist vaporization of the metal and to increase the mean free path in the gas phase of the alkali-metal atoms, reducing the reaction time. On exposure of the apparatus in Figure 1 to the maximum microwave power, a pink argon plasma initially develops throughout the whole apparatus. It was required that the major focus of the plasma was directed toward the alumina crucible containing the alkali metal, both to cause vaporization of the metal and to avoid decomposition of the fullerene which can occur on prolonged exposure to the plasma at high powers (significant decomposition occurs when the C_{60} is exposed directly to the plasma at maximum power for longer than 10 s). Within 5 s, the plasma is predominantly localized around the crucible containing the metal: the C_{60} lies at the diffuse edge of the plasma. A green color in the plasma at this stage is due to carbon in the plasma itself and indicates that the C_{60} is reaching sufficient temperature for sublimation to occur; decomposition is then imminent and the C_{60} is therefore too close to the center of the plasma. Vaporization of the alkali metals Na, K, Rb, and Cs occurs in less than 30 s under these conditions. Our efforts initially concentrated on potassium metal due to its ease of vaporization and the existence of well-characterized potassium intercalate phases of C_{60}. The vessel was designed to allow controlled vaporization of the metal without excessive reduction of the silica walls. Due to the heating effect of the plasma at elevated temperatures the crucible undergoes thermal runaway,[25-27] a consequence of nonlinear absorption of microwave radiation at 2.45 GHz, which aids the rapid vaporization of the alkali metal.

The heat generated by the plasma causes the potassium to vaporize from the alumina crucible, and the resulting potassium atom vapour gives rise to a distinctive purple plasma. Potassium condenses on the cooler surfaces of the vessel including the region where the C_{60} powder is situated. The C_{60} rapidly reacts with the condensed potassium and, under the action of the plasma, intercalation of potassium cations occurs throughout a C_{60} particle forming a K_yC_{60} phase assemblage. Typical values of y range between 4 and 5 depending upon the reaction time. Exposure of C_{60} to a purple potassium discharge (i.e., reaction of C_{60} solid with *uncondensed* potassium in the plasma) for 15 × 5s did not result in uptake of potassium as determined by mass balance and ^{13}C MAS NMR. Increasing the reaction time further or using larger quantities of potassium metal (>100 mg) sometimes resulted in the C_{60} powder being covered in a potassium film, which made separation of the K_yC_{60} phase from the reactor problematic. Occasionally the alumina crucible fractured in the vicinity of the metal, presumably due to thermal shock. A crucible made from zirconia stabilized with 2.8% magnesia caused a more rapid vaporization of metal compared to an alumina crucible because of the more rapid onset of thermal runaway. However fracture of the zirconia crucible in the vicinity of the metal invariably occurred.

Figure 3 shows the ^{13}C MAS NMR spectrum of a K_yC_{60} phase assemblage synthesized by reaction between potassium metal vapor and C_{60} powder in a MIAP. K_4C_{60} and K_6C_{60} are apparent in addition to

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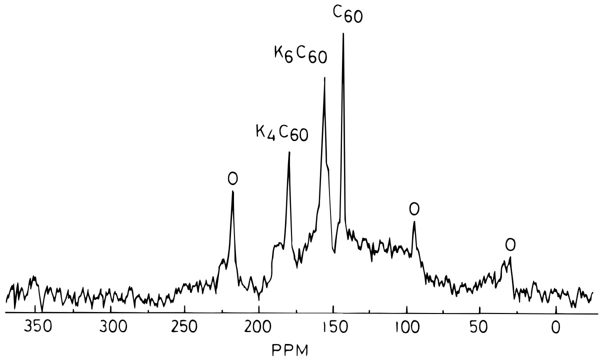

Figure 3. ^{13}C MAS NMR spectrum of a K_yC_{60} phase assemblage prepared using a MIAP. The positions of NMR resonances from known phases are marked. O indicates a spinning sideband.

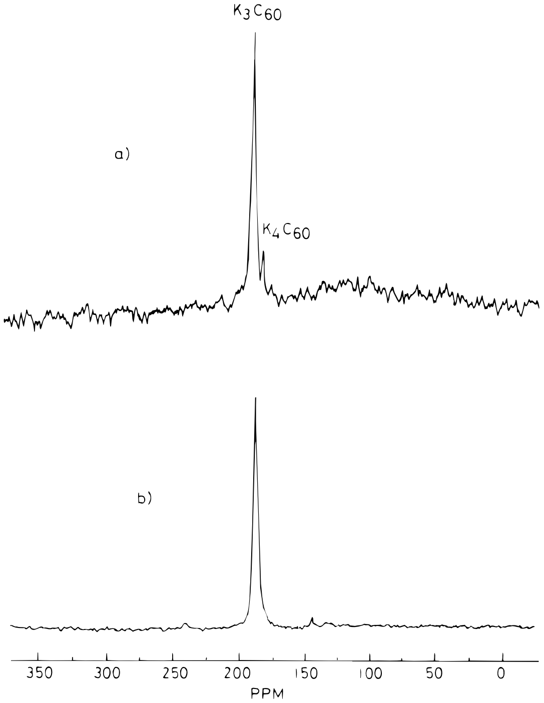

Figure 4. ^{13}C MAS NMR spectrum after exposure of a K_yC_{60} + C_{60} phase assemblage of composition K_3C_{60} to a MIAP: (a) insufficient C_{60} was added to the K_yC_{60} phase assemblage, resulting in the presence of K_4C_{60} impurity and (b) after the correct amount of C_{60} was added to give phase-pure K_3C_{60}.

unreacted C_{60} powder. In the second stage of the microwave synthesis, a pure phase of the desired composition is achieved by adjusting the composition according to the MAS NMR measurements and using the microwave-induced argon plasma to cause rapid reaction of C_{60} with the potassium fullerides, presumably due to diffusion of potassium throughout the C_{60} particles. Addition of the appropriate quantity of C_{60} powder to the K_yC_{60} phase assemblage to obtain a composition of K_3C_{60} followed by exposure to a MIAP for 3 × 5 s gave the ^{13}C MAS NMR spectrum shown in Figure 4a. It can be seen that exposure to a MIAP for a few seconds has caused rapid reaction of the potassium fullerides originally formed in step one with the C_{60} to yield K_3C_{60} and a small amount of K_4C_{60}. This is a consequence of miscalculation of the value of y in the K_yC_{60} assemblage because of poor signal-to-noise in the ^{13}C MAS NMR spectrum used to determine the composition. Addition of a further quantity of C_{60} and subsequent exposure to a MIAP for 2 × 5 s at 10^{-1} mbar

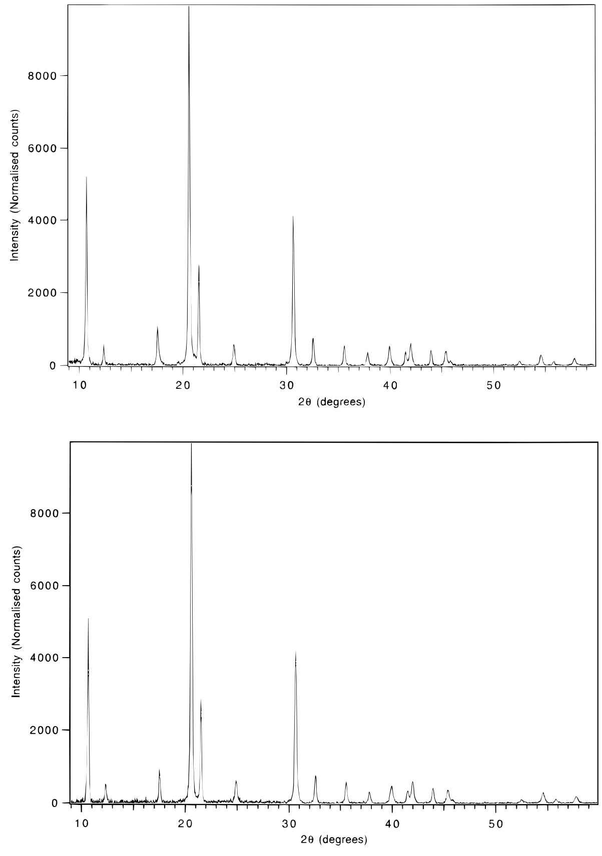

Figure 5. Comparison of X-ray powder diffraction patterns of K_3C_{60} from (a, top) synthesis in a microwave oven and (b, bottom) conventional synthesis in a tube furnace.

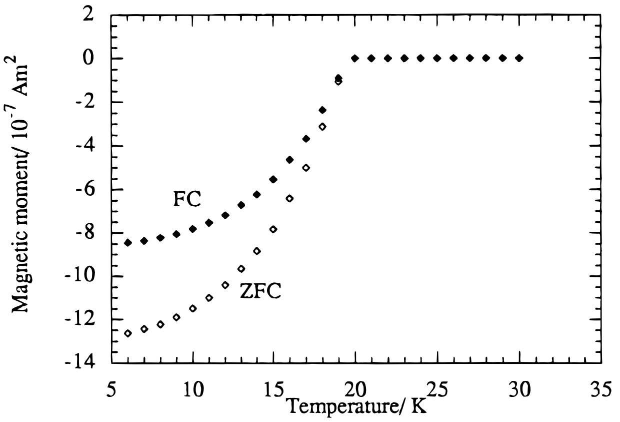

Figure 6. Zero field cooled (ZFC) and field cooled (FC) magnetization in a 10 Oe field as a function of temperature for K_3C_{60} synthesized in a microwave oven.

of argon gave the ^{13}C MAS NMR spectrum shown in Figure 4b. The single peak at δ 187 ppm indicates a K_3C_{60} sample of purity >95%. The powder X-ray diffraction pattern of the K_3C_{60} sample prepared using a MIAP compared to a sample prepared by conventional thermal synthesis is shown in Figure 5. The data sets are essentially identical. Static susceptibility measurements shown in Figure 6 using a SQUID magnetometer revealed a superconducting shielding fraction of 18% (in comparison to typical values of 10−40% obtained in a conventional furnace synthesis).[2] It should be noted that the shielding fraction in alkali-metal fullerides depends strongly on the particle size, as this is usually on the order of the penetration depth.[2] The superconducting transition temperature was 19 K, identical to

Table 1. Alkali-Metal Fulleride Phases Synthesized from A_6C_{60} and C_{60}

composition	Rb_1C_{60}[a]	Cs_1C_{60}[a]	K_3C_{60}	Rb_3C_{60}	K_4C_{60}	Rb_4C_{60}	Cs_4C_{60}
time exposed to MIAP/s	3 × 5	3 × 5	2 × 5	2 × 5	2 × 5	2 × 5	2 × 5
phase purity (MIAP)/%[b]	~96	~97	>99	>99	~97	>99	~95
time in furnace/days	10	10	7	7	7	7	7
phase purity (furnace)/%[b]	>99	>99	>99	>99	>99	>99	>99

[a] Only orthorhombic phases were observed. The fcc rock salt phases formed by quenching from high temperature were not formed. [b] Determined by ^{13}C MASNMR and powder X-ray diffraction. Phase purities less than 99% indicate the presence of C_{60} and/or A_6C_{60} impurities.

that of K_3C_{60} produced in a furnace reaction.[1,28]

The results of MIAP syntheses of various alkali-metal fullerides from A_6C_{60} (where A = K, Rb, and Cs) and C_{60} powder is shown in Table 1. It is apparent that a MIAP can be used very efficiently in the rapid synthesis of alkali-metal fullerides of K, Rb, and Cs. However the MIAP route does not always produce a phase-pure material (probably due to local cold spots) and several annealing steps, with intervening X-ray and MASNMR characterization to indicate the required stoichiometry adjustment, may be required before phase purity is achieved. A conventional thermal reaction is more reliable, although the total reaction time is considerably longer. An alternative synthesis is dilution of the saturated A_6C_{60} alkali-metal phases (A = K, Rb, and Cs), prepared by conventional thermal synthesis with C_{60}, followed by annealing using a MIAP at the full available power for two periods of 5 s. This is considerably more rapid than the thermal annealing stage of the conventional dilution route and is more effective in controlling the stoichiometry of the final product than the direct reaction between the excess alkali metal and the fullerene in the MIAP.

In the case of sodium, where temperatures of at least 450 °C are required for diffusion of sodium cations in the C_{60} host in thermal reactions, a MIAP did not efficiently reproduce the results obtained in a conventional thermal reaction. Synthesis of Na_3C_{60} from Na_6C_{60} and C_{60} showed that exposure to a MIAP for 3 × 5 s in a manner analogous to that used for the preparation of K, Rb, and Cs fullerides caused only partial (~50%) completion of the reaction. Exploration of the microwave synthesis of sodium fullerides did, however, reveal new information about the sodium–C_{60} phase diagram in the region of Na_1C_{60}. Na_2C_{60} and C_{60} in equivalent quantities were exposed to a MIAP for 3 × 5 s in a manner analogous to the reactions of K, Rb, and Cs fullerides in an attempt to prepare Na_1C_{60}. ^{13}C MAS NMR spectroscopy of the product showed that no reaction appeared to have taken place; two peaks at δ 143 and 172 ppm, corresponding to the chemical shifts of the C_{60} and Na_2C_{60} starting materials, respectively, were observed. With the other half of the Na_1C_{60} composition, conventional thermal synthesis in an evacuated stainless steel tube was performed at 500 °C for 7 days with identical results. A second sample of equimolar quantities of Na_2C_{60} and C_{60} sealed in tantalum under an atmosphere of helium was also heated to 600 °C for several days with no indication of reaction, as observed by ^{13}C MAS NMR (see Figure 7). However, a polymeric Na_1C_{60} phase or a phase with rapid nuclear spin relaxation would not be detectable by NMR.

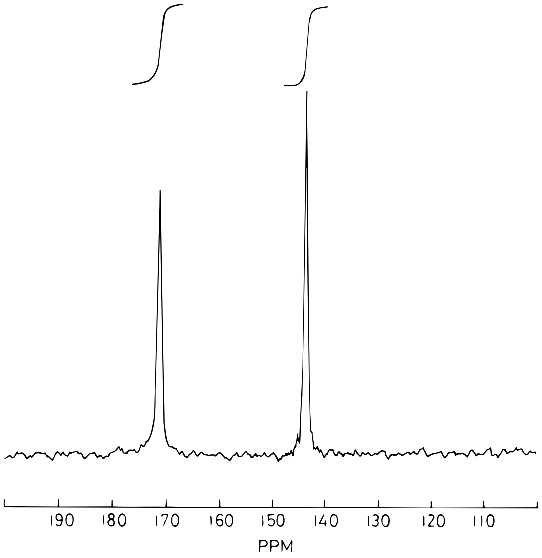

Figure 7. ^{13}C MAS NMR of a sample of composition Na_1C_{60} (prepared by heating an equimolar mixture of Na_2C_{60} and C_{60} to 600 °C over several days). The integration shows that equimolar quantities of C_{60} and Na_2C_{60} are present.

In contrast to the evidence for phase separation from NMR, visual inspection of powder X-ray diffraction data did not show evidence for a two-phase mixture, as shown in Figure 8. The reflections were indexable as a single phase of $Pa\bar{3}$ symmetry and were not broader than the Bragg peaks from pure Na_2C_{60} or C_{60}. However, the small differences in the lattice parameters of Na_2C_{60} and C_{60} can account for this observation, which is similar to the conflict between NMR, PES, and X-ray diffraction data for the K_xC_{60} system.[29] At room temperature, $K_{1.5}C_{60}$ appears to be a single phase to powder X-ray diffraction but can clearly be seen to be a two-phase mixture of K_3C_{60} and C_{60} in the ^{13}C NMR spectrum. We carried out a series of profile refinements to investigate this apparent discrepancy between the two techniques. The single phase hypothesis was tested in a model independent manner by carrying out a Le Bail intensity extraction,[30] in which the structure factors of the allowed Bragg reflections are treated as variables. The residual thus corresponds to the best fit which can be attained by a profile refinement assuming a single phase. The Le Bail extraction with a single phase of $Pa\bar{3}$ symmetry gave a reasonable fit with $\chi^2 = 5.89$ and a lattice parameter of 14.1868(5) Å. A one-phase Rietveld refinement of a $Pa\bar{3}$ symmetry Na_1C_{60} phase gave $\chi^2 = 10.1$. Rietveld refinement of the Na_1C_{60} composition (Figure 8), using a *two-phase* model of an equimolar mixture of $Pa\bar{3}$ symmetry Na_2C_{60} and $Fm\bar{3}m$

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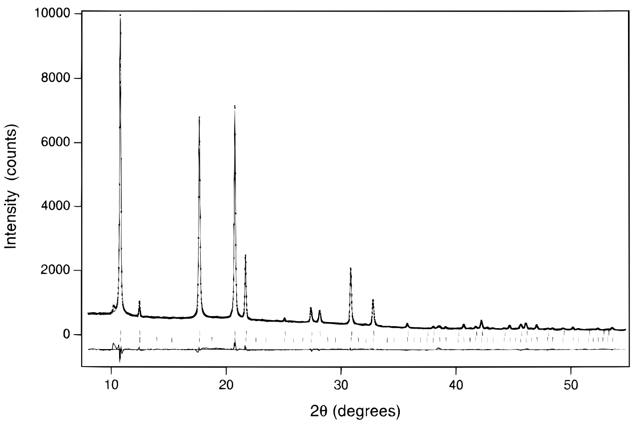

Figure 8. Rietveld refinement of the powder X-ray diffraction pattern of the Na_1C_{60} sample from Figure 7. The model used for the refinement is 50 mol % Na_2C_{60} and 50 mol % C_{60} (these fractions were fixed and not refined). The refined lattice parameters of the Na_2C_{60} and C_{60} phases were 14.1926(4) and 14.1685(7) Å, respectively. In Na_2C_{60}, $U_C = 0.03$ Å^2, $U_{Na(oct)} = 0.13$ Å^2, $U_{Na(tet)} = 0.02$ Å^2 Na(tet) on 8c x,x,x $x = 0.2477(7)$ $f = 0.94$ Na(oct) on 4b $^1/_2$, $^1/_2$, $^1/_2$ $f = 0.12$. $R_w = 4.02\%$ $R_E = 2.08\%$. The observed data are shown as points, the calculated model is a solid line, and the difference curve is plotted below the fit on the same scale. The ticks mark the predicted positions of the Bragg reflections from the C_{60} (upper ticks) and the Na_2C_{60} (lower ticks) phases. In the Rietveld refinements, only one setting angle of the $C_{60}{}^{2-}$ anion around the [111] direction was used, ignoring the possibility of the presence of multiple orientations of the anion.

symmetry C_{60} (in accord with the NMR results) gave a slightly better fit than the one phase Le Bail extraction ($\chi^2 = 3.7$), with lattice parameters of 14.1926(4) and 14.1685(7) Å for the two phases. Addition of dry degassed toluene to a portion of the Na_1C_{60} sample gave a black residue of Na_2C_{60} (as confirmed by ^{13}C MAS NMR) and a purple supernatant of C_{60}, giving chemical evidence for the phase separation suggested by the physical measurements. Solid solution behavior has been proposed for the Na_xC_{60} system at room temperature where $1 \leq x \leq 3$.[9] Temperatures up to a maximum of ca. 500 °C for 3 days were used in the synthesis, but a detailed description of the preparation was not given. A recent report[31] on the phase diagram and thermodynamics of sodium fullerides derived from electrochemical data at 326 °C showed that solid solution behavior in the Na_xC_{60} system was not present below $x = 2$ but was present between 2 and 3. We attempted preparation of solid solution sodium fullerides between $x = 1$ and 2 by quenching reactions from 500 °C in oil at room temperature but obtained identical results to those above. The synthetic routes which we have described here produce phase separation at the Na_1C_{60} composition.

Discussion

We have described how a MIAP can be used for the rapid synthesis of a variety of phase-pure alkali-metal fullerides. There are two principal mechanisms which would allow the microwaves and the plasma which they induce in the argon medium to greatly accelerate the rate of formation of the metal fullerides—microwave dielectric loss heating and the thermal effect of the ions, electrons, and neutral molecules in the plasma itself. In contrast to the vast majority of microwave syntheses, the reaction is not directly accelerated by the dielectric loss mechanism (absorption of energy by the reaction component(s) to impart energy to the system). Test reactions showed small quantities of potassium metal, C_{60} powder (in step one) and the A_yC_{60} phase assemblages in step two of the reaction pathway (where A = Na, K, Rb, and Cs) do *not* absorb microwave radiation at 2.45 GHz. The presence of the argon gas in the tube is critical for the success of the synthesis, and in the following paragraphs we outline evidence supporting the proposal that the thermal action of the plasma is responsible for the rapid synthesis.

A MIAP immerses the reaction components in an ionized gas, generating heat due to continual bombardment of ions and electrons on the surface of the solid reagents by transfer of the kinetic energy of these particles (greater than 10 eV/electron at 2.45 GHz[32]). The widths of the X-ray Bragg reflections are similar in samples prepared by both thermal and microwave techniques, showing that the surface bombardment does not affect the size of the crystalline domains. In the first step, which involves transport of the alkali metal to the C_{60} particles, a substantial gas-phase concentration of potassium is required. The MIAP produces this by rapidly heating the potassium, both directly and by preheating the ceramic “furnace” to allow thermal runaway by microwave dielectric absorption by the alumina at high temperature. Rapid intercalation to form the range of potassium fullerides seen in the MAS NMR spectra after the first step may then be due to the concentration of energetic potassium species in the plasma itself (C_{60} does not react with the potassium plasma alone in the absence of potassium condensed on the C_{60} particles, however). The mechanism that we favor is rapid potassium heating leading to condensation of potassium liquid onto the C_{60} particles: the location of the C_{60} solid in the periphery of the plasma raises it to a sufficient temperature to allow rapid intercalation. This would explain why reaction with large excesses of potassium leads to condensation of potassium onto the product surface once full reaction to form K_6C_{60} is complete. Although direct microwave absorption is not involved, it is also possible that preheating by the plasma allows dielectric loss heating to occur at high temperature, in a similar manner to the thermal runaway observed in ceramics.

The rapidity of the second, annealing stage, in which no excess potassium is present and the action of the plasma is to cause reaction between alkali-metal fullerides and C_{60}, may also be understood in terms of effective local heating by the plasma. The contrast with a conventional furnace synthesis is that the source of heating is located inside the reaction vessel itself, reducing the requirement to raise the vessel to a high temperature in order to heat the reagents (although the vessel reaches a temperature of at least 150 °C during the annealing step). A more exotic possibility is that the diffusion and homogenization of the alkali-metal cations is driven by capture of electrons from the plasma by the neutral C_{60} molecules in the initial, inhomogeneous sample, which causes rapid diffusion of the

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potassium cations between particles driven by the electrostatic field thus produced. This has some precedent in the mechanism of plasma polymerization synthesis of solid films, where radicals are produced by electron capture from the plasma both by monomer molecules in the gas phase and on the solid surface.[15]

It is clear that sodium diffusion is slower in fullerides than that of potassium, rubidium, and cesium in both thermal and MIAP-induced reactions. There are several possible reasons for this: the close size match between a sodium cation (radius = 0.97 Å) and a tetrahedral site (radius = 1.02 Å) in the fcc C_{60} lattice, stronger covalent interaction between sodium and C_{60} than is the case with the heavier, more electropositive alkali metals or the differing structural chemistry of the alkali-metal-saturated fulleride phases. Sodium, unlike the larger alkalies, does not form body-centered cubic (bcc) saturated A_6C_{60} phases. The fulleride packing in the bcc phases is less dense, and this may allow more efficient diffusion of the heavier alkali metals if they react by initial formation of the saturated phase. The failure of the MIAP to reproduce the thermal results suggests that the temperatures achieved at the sample position in the plasma are less than 450 °C, which seems to be optimal to induce complete thermal reaction in the sodium$-C_{60}$ system. The observation that sodium diffusion is sluggish in both the microwave and conventional syntheses is good evidence for a purely thermal mechanism for the action of the MIAP, and allows us to place an upper limit on the temperature reached by the sample under the microwave reaction conditions of 450 °C.

Comparison with samples produced conventionally in a furnace shows that a MIAP is not as reliable in producing a phase-pure material, although the total reaction time is considerably reduced. The major reason for this is probably local temperature variations throughout the bulk of the sample. The simplest method to combine the rapidity of the microwave reaction with the reliability of the thermal route is to react A_6C_{60}, prepared in a furnace reaction and characterized by X-ray and NMR techniques for phase purity, with C_{60} in the microwave apparatus.

Argon plasmas were used in the synthesis as they have greater stability than dinitrogen plasmas at the pressures and volumes used in this study: the relatively low temperatures produced by the monatomic gas plasmas are advantageous in avoiding fullerene decomposition. The use of other gases, in particular diatomics such as nitrogen which have been shown to allow access to higher temperatures,[18] is a possible method of effecting more rapid sodium diffusion to overcome the problems in sodium fulleride synthesis apparent in this study, though more stringent control of temperature homogeneity in the reaction vessel would be required. Thermal and MIAP reactions both indicate that Na_2C_{60} is the lower boundary in the Na_xC_{60} phase diagram at room temperature and pressure. Rietveld analysis of the powder X-ray data is consistent with the MAS NMR observations, though the refined lattice parameters from the two-phase refinement suggest that the C_{60} and Na_2C_{60} formed at the Na_1C_{60} composition differs slightly over the X-ray length scale from the pristine solids: however, it is difficult to derive accurate lattice parameters from the two-phase refinement as no separation of the Bragg peaks from the two phases is observed. The stability of Na_2C_{60} may be rationalized chemically in terms of the particularly good size match between the sodium cation and the tetrahedral site.

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