Rapid Synthesis of Phase Pure K_3C_{60} using a Microwave-induced Argon Plasma

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Superconducting alkali metal fullerides can be synthesized in less than 60 s reaction time using a microwave-induced argon plasma; the rapid synthesis of K_3C_{60} is described.

Since the discovery of superconductivity in K_3C_{60},[1] alkali metal fullerides have been the focus of much attention. The synthesis of phase pure alkali metal fullerides requires several days reaction and annealing at temperatures of the order of 350 °C, and is achieved by direct reaction with stoichiometric quantities of metal or dilution of saturated A_xC_{60} compositions. Alternative routes to obtain the desired stoichiometry have been reported but there is no significant reduction in the total time to obtain phase purity as several days are required to anneal the sample.[2,3]

Synthesis using microwave radiation has been explored in both solution and solid state reactions due to the short reaction times employed compared to conventional thermal reactions.[4] Absorption of the microwave radiation is required by at least one of the reaction components or the solvent medium. The heating mechanism is *via* dielectric or occasionally conduction losses. Here we report the bulk synthesis of phase pure K_3C_{60} in a total reaction time of under 60 s using a microwave induced argon plasma generated in a conventional microwave oven. To the best of our knowledge this is the first example of the use of a microwave induced plasma in macroscopic chemical synthesis.

The 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. Reaction vessels were supported on fire bricks to mitigate against thermal contact with the oven walls.

The synthesis of phase pure K_3C_{60} using microwave radiation is performed in two separate steps: an initial reaction of the metal with the C_{60} powder which produces a mixture of C_{60} and K_yC_{60}, and a final annealing stage.

The reaction vessel is shown in Fig. 1. An argon plasma is readily generated in a microwave oven affording a green glow in the vessel and causing a rapid rise in temperature, depending on the power applied.[5] Powers of a few tens of watts are typically needed to induce plasma formation, depending on the pressure of argon and the geometry of the vessel. In this case the vessel was designed to allow controlled vapourisation of the metal without excessive reduction of the silica walls. An alumina crucible was used to restrict violent vapourisation of the metal and subsequent reduction of the silica vessel. The vessel was placed under argon at 10^{-5} mbar, to assist vapourisation of the metal and the plasma was initiated by application of the microwaves. The focus of the

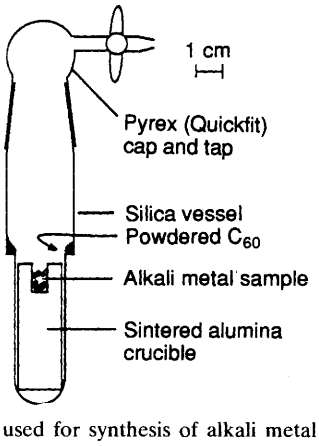

Fig. 1 Apparatus used for synthesis of alkali metal fullerides using microwave radiation

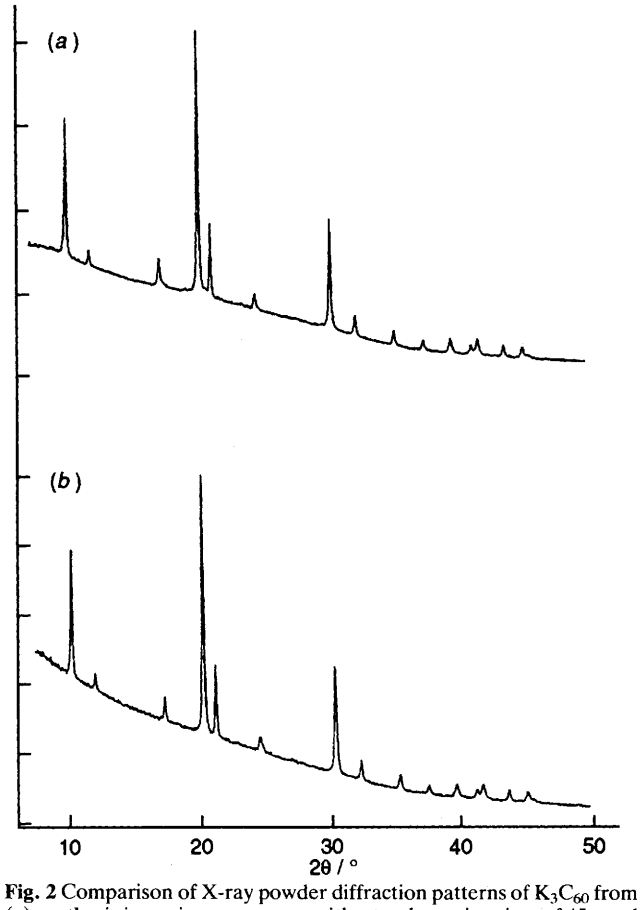

Fig. 2 Comparison of X-ray powder diffraction patterns of K_3C_{60} from (*a*) synthesis in a microwave oven with a total reaction time of 45 s and (*b*) conventionally in a tube furnace over 14 d at 350 °C. Data were collected in transmission geometry on samples sealed in 0.5 mm capillaries using a Siemens D5000 instrument with a position sensitive detector and Cu-Kα_1 radiation.

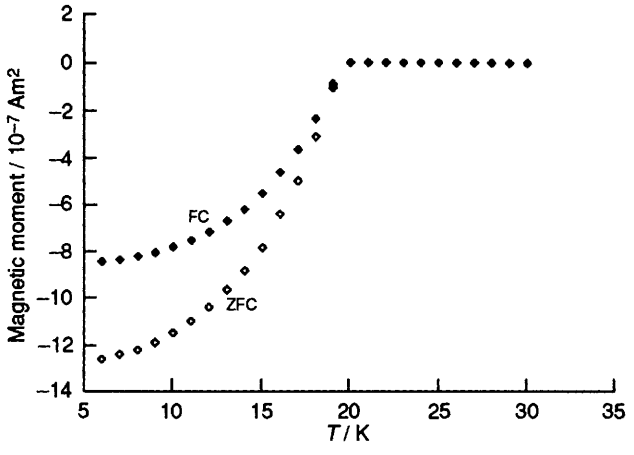

Fig. 3 Zero field cooled (ZFC) and field cooled (FC) (10 G) magnetization as a function of temperature for 2.6 mg of K_3C_{60} synthesised in a microwave oven and sealed in a quartz capillary under helium. Measurements were performed in a Cryogenic Consultants S600C SQUID magnetometer.

plasma was controlled by positioning the reaction vessel at an antinode or node in the oven cavity. It was required that the major focus of the plasma was directed toward the alumina crucible to aid vapourisation of the metal and simultaneously to avoid decomposition of the fullerene which can occur on prolonged exposure to the plasma at high powers. The heat generated by the plasma causes the potassium to vapourise from the alumina crucible, and the resulting potassium atom vapour gives rise to a distinctive purple plasma. The C_{60} rapidly reacts with this potassium vapour.

A typical reaction time for 50 mg of C_{60} and 100 mg of potassium is 30 s. The composition of the resulting K_yC_{60} phase assemblage was determined *via* ^{13}C MASNMR by integration of the relevant peaks corresponding to the known phases in the K_xC_{60} phase diagram (x = 3, 4 and 6).† Typical values of y range between 4 and 5 depending upon the reaction time.

The sample was then intimately mixed with a further quantity of C_{60} required to give the composition K_3C_{60} and the mixture subjected to heating *via* an argon plasma for approximately 10 s. This operation was performed in a Pyrex tube sealed with a Teflon stopcock under a convenient argon pressure of 10^{-1} mbar. Analysis of the annealed product by ^{13}C MASNMR and X-ray powder diffraction revealed no perceptible difference from that of a sample of K_3C_{60} produced conventionally using a tube furnace over a 14 d period (Fig. 2). SQUID magnetometry revealed a superconducting shielding fraction of 18% (in comparison to typical values of 10–40% obtained in conventional furnace syntheses) (Fig. 3). The superconducting transition temperature (T_c) was 19 K, identical to that of K_3C_{60} produced in a furnace reaction. K_3C_{60} could also be prepared by subjecting a mixture of K_6C_{60} (produced conventionally in a furnace)[6] and C_{60} in a 1 : 1 ratio, to an argon plasma for 10 s. Other alkali metal phases were also readily synthesised by the same method *e.g.* Rb_3C_{60}, Rb_4C_{60} and Cs_4C_{60}.

In the absence of the argon plasma vapourisation, the intercalation reaction and annealing does not occur. This is because neither C_{60} nor potassium metal absorbs microwave radiation to any significant extent at the frequency employed.

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† ^{13}C MASNMR was performed at 50.32 MHz to an external reference of adamantane. Integration was performed by the cut and weigh method. Samples were contained in a KEL-F insert within a 7 mm zirconia rotor and spun typically at *ca.* 3 kHz.

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