



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application**:

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Structural investigation and thermal stability of the alkaline-earth intercalated fullerene polymer Mg_5C_{60}	Experiment number: CH- 2715
Beamline: ID31	Date of experiment: from: 31.01.2009 to: 03.02.2009	Date of report: 09.02.2009
Shifts: 9	Local contact(s): Dr. Irene Margiolaki	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr Daniele PONTIROLI* Dr Mauro RICCÒ*		

Report:

Intercalated fullerene polymers represent a wide, but still rather unknown family of compounds, which display a wealth of structural architectures (1D linear or zigzag chains, 2D planar sheets, where C_{60} units could be connected by single C-C bonds, four-membered carbon rings ([2+2] cycloaddition reaction) or both [1,2]). An important parameter which influences the polymerisation is the size of the intercalant: usually, in alkali doped fullerenes, the formation of intermolecular bonds is favoured when the lightest atoms are intercalated. This rule is valid also when the alkali-earth fullerenes are considered; among them, those obtained with magnesium are then good candidates for the production of polymers.

We succeeded in preparing the series of Mg_xC_{60} compounds ($2 \leq x \leq 6$), following a new synthesis technique based on the use of a metallorganic precursor, which allowed us to drastically reduce the duration of the sample preparation, as compared to the earlier efforts [3]. The samples were then sealed in quartz capillaries of 0.5 mm diameter and underwent high resolution synchrotron diffraction at ID31 beamline ($\lambda = 0.7999(1) \text{ \AA}$). Data were collected both at room and at high temperature, by heating the capillaries with a hot gas blower, capable to reach $T = 800\text{K}$.

The diffraction patterns at room temperature show quite broad lorentian peaks, the main contribution of which is due to the size and strain effects arising from the sample. In particular, the typical diffraction profile consists in the overlap of the reflections of at least two different phases: i) the former (χ phase) is easily indexed with the rhombohedral cell proposed by Borondics et al. [3] (s.g. $R-3m$, $a = 9.229(1) \text{ \AA}$, $c = 25.145(5) \text{ \AA}$, $\gamma = 120^\circ$); ii) the latter (δ phase) is completely new and is indexed with a monoclinic cell, very similar to that of polymer Li_4C_{60} (s. g. $I2/m$, $a = 9.309(2) \text{ \AA}$, $b = 9.036(1) \text{ \AA}$, $c = 14.798(4) \text{ \AA}$, $\beta = 91.68(1)^\circ$). In some cases, a minor amount of unreacted C_{60} is also observed. The Le Bail pattern decomposition of the diffraction profile of Mg_4C_{60} , where all the three phases are present, is shown in **Figure 1a**.

Although the Mg_xC_{60} compounds obtained with the metallorganic precursor do not show significant changes in the diffraction profiles by tuning the Mg stoichiometry, we found indications that the δ phase is compatible with a lower amount of Mg. This hypothesis seems to be clearly confirmed by the preliminary

diffraction analysis of Mg_xC_{60} synthesized via the “standard” route [3], where both χ and δ pure phases could be obtained with the stoichiometries respectively $x = 2$ and $x = 5$.

The Rietveld refinement of the two Mg_xC_{60} structures is still in progress, due to the difficulties arising from the superimposing peaks of the two phases and it would deserve a continuation of the experiment. Preliminary analysis, however, has clearly shown that in both the two phases fullerenes are polymerised. The χ “high doped” Mg_xC_{60} phase strongly resembles that of high pressure Rh- C_{60} , in which 2D polymeric planes (ab planes) are formed by highly distorted C_{60} units, connected with four-membered carbon rings. The diffraction pattern shows high anisotropic broadening of the reflections, which varies from sample to sample; this effect indicates the presence of a relevant disorder (stacking faults, structural defects) and prevented a detailed structural analysis so far. On the contrary, the δ “low doped” phase is better crystalline with very sharp reflections. Similarly to Li_4C_{60} , C_{60} polymeric chains connected by four membered carbon rings propagate along the shortest b axis, while the particular arrangement of the chains is such that pairs of carbon atoms of neighbouring fullerenes are placed very close (~ 2 Å), suggesting the presence of further intermolecular single C-C bond along the a axis, thus forming a 2D “hybrid” network. Preliminary analysis also suggests that the two Mg^{2+} ions should be placed in the pseudo-tetrahedral site of the monoclinic cell, again in strong analogy with Li_4C_{60} .

Mg_4C_{60} underwent then high resolution powder diffraction during a thermal annealing up to $T = 800\text{K}$. Surprisingly, we found that both the χ and δ phases are exceptionally stable. Indeed, their reflections disappeared at the same time when the C_{60} peaks dropped out, due to the cage collapse and the carbon graphitisation, observed at $T = \sim 800\text{K}$, thus confirming the previous evidences arising from ESR study [4]. The temperature dependence of the lattice constants are in agreement with the polymeric nature of the compound and provided also a detailed confirm of the bond features: the linear thermal expansion along the a axis in the χ cell is approximately equal to that along b axis in the δ cell and 4-5 times smaller than that along c axis (stacking axis) of both the phases. On the contrary, the expansion along the a axis of the δ cell is slightly smaller than along b (see **Figure 1b**), accordingly with the two different bonding motives.

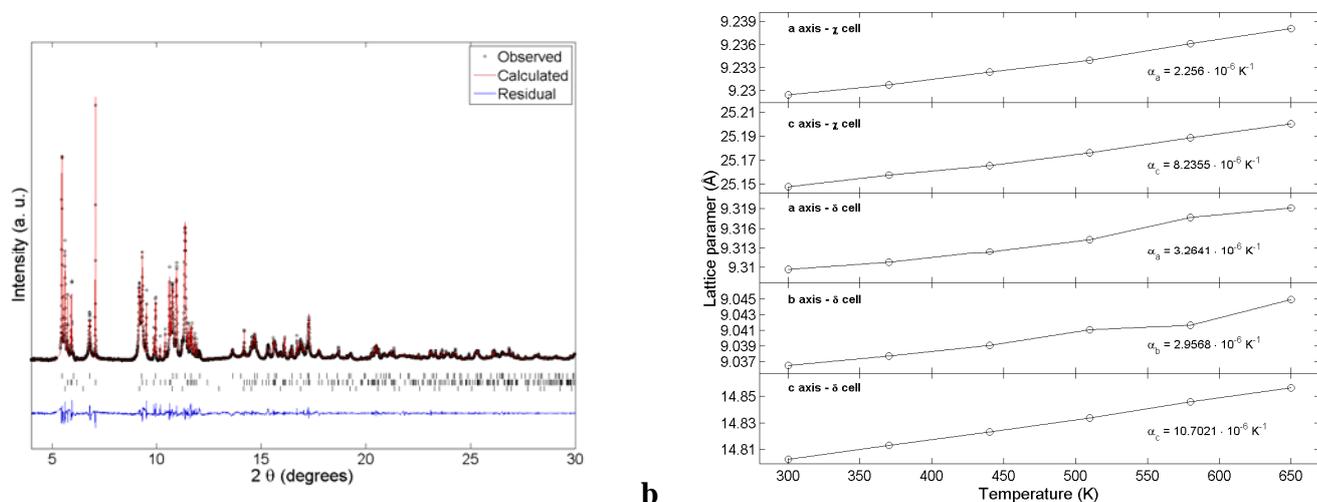


Figure 1: **a)** Observed (o) and calculated (solid red line) powder diffraction pattern of Mg_4C_{60} at 300 K; the sample is a mixture of two polymer phases, rhombohedral (χ) and monoclinic (δ), with a small fraction of unreacted C_{60} (Le Bail analysis, R_{wp} 3.66%). **b)** Temperature dependence and linear thermal expansion coefficients of the lattice parameter of the χ and δ phases in Mg_4C_{60} , in the temperature range $T = 300\text{-}650$ K. The lines through the data points are guides to the eye.

References

1. S. Margadonna et al., *J. Am. Chem. Soc.* **126** (2004), 15032; M. Riccò, et al., *Phys. Rev. B* **72** (2005), 155437.
2. M. Riccò et al., *J. Am. Chem. Soc.* DOI: 10.1021/ja909614x, Publication Date (Web): Jan. 26, 2010.
3. F. Borondics et al., *Sol. State Comm.* **127**, 311 (2003).
4. D. Quintavalle et al., *Phys. Rev. B* **77**, 155431 (2008).