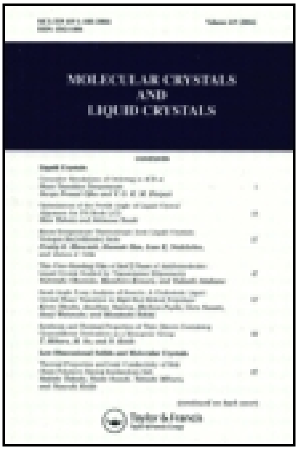

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Phase Transitions and Chemical Transformation in Lithium Fullerides Li_nC_{60}

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Phase Transitions and Chemical Transformation in Lithium Fullerides Li_nC_{60}

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Systematic studies were carried out on the properties of lithium fullerides Li_nC_{60} ($0<n\leq30$) prepared by two different methods: thermal synthesis at ambient pressure and in the temperature range 455÷473 K, and solid phase synthesis at 2.3 GPa and room temperature.

Keywords: lithium fullerides; IR spectra; polymeric structures

INTRODUCTION

The Li_nC_{60} system seems to have a very rich phase diagram. Small ionic radius Li^+ permits the formation of lithium clusters in the octahedral intestitial voids of fullerite yielding compounds with great lithium content. Alkali metal diffusion into C_{60} by application under high pressures leads to the formation of lithium fulleides Li_nC_{60} with $n\leq27$ [1]. We have shown that even under thermal synthesis condition at ambient pressure the maximal content of Li corresponds to composition of $Li_{30}C_{60}$ [2]. Thermal or liquid-phase synthesis in the field of $Li_{n<3}C_{60}$ compositions yields a solid intercalation solution. A further increase in lithium concentration up to n=12 results in the formation of intercalates of different structures involving lithium clusters, while fullerene molecules are polymerized to a different degree[3]. Up to now we have very little experimental knowledge of the structure and phase equilibrium wich are realized in Li_nC_{60} system.

EXPERIMENTAL

This paper studies lithium fullerides prepared by two different methods: thermal synthesis at ambient pressure and in the temperature range 455÷473 K, and solid phase synthesis at 2.3 GPa and room temperature. Detailed description is presented in[4]. X-ray diffraction analyses were performed with FR-552 diffractometer with CuK$_\alpha$ radiation. IR spectra were obtained by using an UR-20 spectrometer.

RESULTS AND DISCUSSION

Thermal synthesized lithium fullerides

The samples in the interval of composition Li_nC_{60}, $0 \leq n \leq 30$, were obtained by liquid-phase technique. We discussed IR spectra of such samples with n<12 in our previous work [3], for n>12 are displayed in Fig. 1.

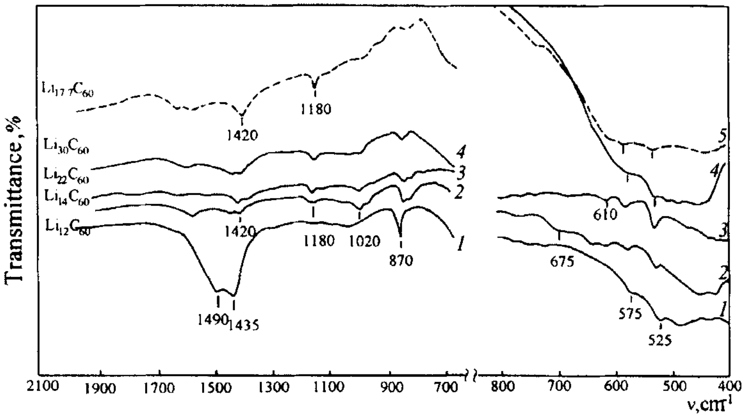

FIGURE 1 IR spectra of thermal synthesized Li_nC_{60}. Spectrum of $Li_{17.7}C_{60}$ was made after heating of sample up to 753K.

The X-ray diffraction data on the samples with n>12 indicate monoclinic (M) and cubic (with less parameter that for fcc C_{60}) phases. IR spectra are characterized by much low intensity of IR active modes of pristine C_{60} and polymeric forms (700-800 cm^{-1})[5], appearance of two maxims of the Li-Li absorption band (860 and 870 cm^{-1}) and the band at 675 cm^{-1} attributed to Li–C vibrations[6]. That is further increase in the lithium concentration in fulleride leads to destruction of C_{60}–C_{60} bonds and changing the Li–Li bond type. Li-C bond vibrations correspond to interaction of Li with "aromatic" carbon rings of

C_{60}. Account all the data we propose that addition Li doping (n>12) leads to destruction of polymeric forms into several phases, where C_{60} exists in both monomer or dimer form and Li clusters occupy not only octahedral sites but also tetrahedral.

When heating samples Li_nC_{60} n>12 up to 713–753 K we have registered exothermic effect on the DTA thermograms. The reversible transformation with an endothermic effect at 721±5 K was an evidence to the lithium carbide formation. X-ray patterns have shown a mixture of Li_2C_2 and fcc C_{60}. The IR spectrum of finished product for the sample of $Li_{17.7}C_{60}$ stoichiometry is displayed in Fig.1. The volumetric analysis of this system results in the molar volume of 512±5 cm^3/mol C_{60}, wich is very close to calculated datum from the reaction $Li_{17.7}C_{60} \rightarrow 8.85Li_2C_2+0.7C_{60}$ (508cm^3/molC_{60}). Thus thermal destruction of Li_nC_{60} (n>12) takes place under heating up to 713–753 K and Li almost completely releases from the fullerene matrix with formation of well crystallized Li_2C_2.

Lithium fullerides synthesized under high pressure (HP)

The samples of the composition Li_nC_{60} $2.1 \leq n \leq 10.1$ were synthesized by solid-phase method under HP, corresponding IR spectra are shown in Fig.2.

The IR spectrum of $Li_{2.1}C_{60}$ sample (Fig.2) testifies the formation of orthorhombic (O) polymer (absorption bands at 1100cm^{-1} and the ratio of bands intensity in the region 700-800cm^{-1} [5]). X-ray diffraction data of Li_nC_{60} 2<n<3 indicated the formation of O phase also (***a***=9.128(5) Å; ***b***=9.915(6) Å; *c*=14.71(1) Å). Inside chains C_{60}–C_{60} distance (9.128(5)Å) is slightly smaller than that in the fullerene O polymer (***a***=9.26Å[5]). It is probably caused by formation of lithium clusters between C_{60} polymeric chains what was confirmed by the presence of Li–Li band at 870cm^{-1} [6] in the IR spectrum.

In the spectrum of $Li_{3.1}C_{60}$ (Fig. 2) the intensity of the absorption band at 870 cm^{-1} decreases. The sample has the O lattice modification with traces of fcc. The absorption bands characteristic for polymeric forms of C_{60} (the sharp band at 610 cm^{-1} and low intensity bands in the region 700-800 cm^{-1}) testifies a possibility of existence of orthorhombic and possible cubic phases. We suggest that for sample of such stoicheometry a mixture of polymeric phase with lithium clusters between C_{60} chains and the cubic phase in which three Li atoms are homogeneously distributed over fcc sites is formed.

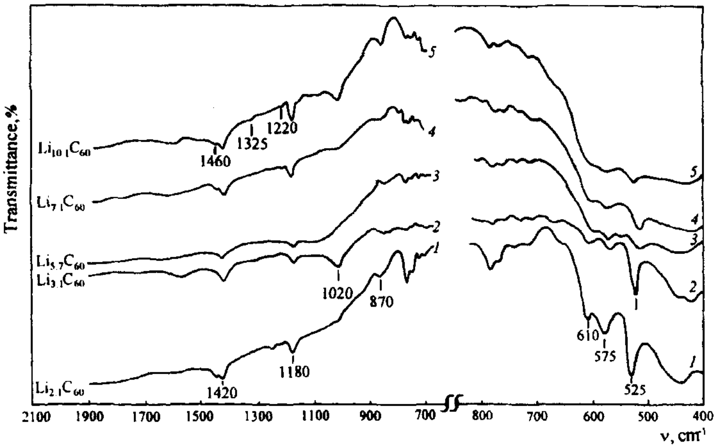

FIGURE 2 IR spectra of Li_nC_{60} synthesized under high pressure

X-ray patterns of the fullerides $Li_{5.7}C_{60}$ and $Li_{7.1}C_{60}$ correspond to the triclinic (Tk) lattice, parameters are shown in Table 1. In the IR spectra of these samples the decrease of bands' intensity of C_{60} molecule and increase of bands' intensity of polymeric forms have observed. (Fig.2). The intensity of the absorption band at 870 cm^{-1} increases with increasing of n. It is likely Tk lithium fullerides were formed by fullerene dimers like those that were fixed in K_1C_{60} and Rb_1C_{60} fullerides with lithium clusters between them (Fig.3). Minimum interfullerene distance 9.34Å corresponds to C_{60}-C_{60} dimer bond. After several days of storage the dimer phase of Li_nC_{60} as well as in K_1C_{60} and Rb_1C_{60} was transformed in the polymeric O phase with the parameters identical to those in $Li_{2.1}C_{60}$ sample (a = 9.11(1)Å, b = 9.87(1)Å, c = 14.76(2)Å).

TABLE 1 X-ray data for dimer structures of K_1C_{60}, Rb_1C_{60}[7] and Li_nC_{60} (triclinic modification).

Parameters and angles	dimer K_1C_{60} orthorhombic [7]	dimer Rb_1C_{60} orthorhombic [7]	Li_nC_{60} triclinic
a	9.63 Å	9.61 Å	9.695(2) Å
b	9.92 Å	9.79 Å	9.965(2) Å
c	14.15 Å	14.19 Å	16.694(5) Å
α	90°	90°	86.62(2) °
β	90°	90°	99.77(3) °
γ	90°	90°	114.75(2) °

In some cases X-ray patterns indicated a mixture of Tk and fcc (with less parameter that for pristine C_{60}) what infers that the transformation to the polymeric phase occurs through the intermediate fcc phase.

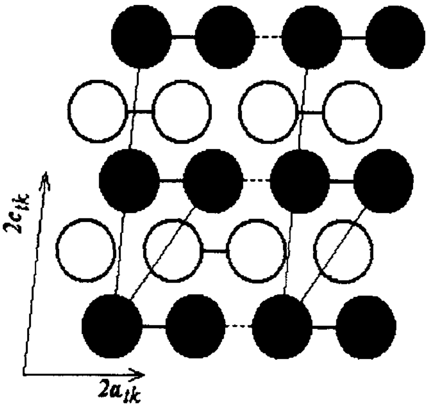

FIGURE 3 The ac projection of the 2a,b,2c supercell of triclinic Li_nC_{60}. Only the position of the C_{60} molecules and the dimers bonds are shown.

Increase of n up to 10.1 leads to further decrease of bands' intensity of C_{60} molecule (Fig. 2). The $F_{1u}(3)$ and $F_{1u}(4)$ vibration modes are split by the change of double bonds state. The bands at 1220, 1325, 1460 cm^{-1} are observed in the IR spectrum of $Li_{10.1}C_{60}$. The intensity of the band at 870 cm^{-1} is comparable with intensity of bands at 1180 and 1425 cm^{-1}. Our X-ray results indicate the existence of M phase like in thermal synthesized Li_nC_{60} (n>9). X-ray patterns registered after 10 hours and 1 day indicate the transition to Tk phase and O phase correspondingly with traces of Li. IR spectrum of $Li_{10.1}C_{60}$ registered after a day of sample storage under Ar atmosphere hasn't shown any differences from the first IR spectrum of this sample. It is possible that the lithium evolution caused either by the X-ray radiation ore by enviroment. Locating of large Li cluster between C_{60} dimers gives rise to increasing repulsion potential due to overlap between alkali ion core and carbon orbitals which can promote Li evolution from the dimer M structure.

Thus we can suggest the following scheme of phase transitions in Li_nC_{60} synthesized under HP with increasing of n. Doping of small amount of Li $2<n<3$ leads to formation of one-dimension (1D) O polymer. Furver increase of metal doping gives rise to formation of mixture of dimer and polymer phases caused by increase of lithium concentration. When n reaches the volume of 5.7 only dimer structure is created. Increase of metal concentration up to certain n in the region $7.1 \leq n \leq 10.1$ leads to formation of monoclinic phase where the fullerene dimers are surrounded by large lithium clusters.

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