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Synthesis and Investigation of Boron-Doped Fullerene and Scandium-Containing Fullerene

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Abstract—We report on the plasmachemical synthesis of fullerene derivatives containing boron and scandium. The synthesis was conducted at atmospheric pressure in a carbon–helium plasma jet generated by an RF arc. © *2003 MAIK "Nauka/Interperiodica".*

Originally, $C_{(60-x)}B_x$ (x = 1–6) molecules were observed by Smalley *et al.* [1] in the gas phase. Muhr *et al.* [2] succeeded in isolating a very small amount of born-containing heterofullerenes from a soot sythesized by the Krätschmer–Haffman method using graphite rods with boron, boron nitride, or boron carbide additives. Boron-containing fragments of the C_nB type (with n = 59, 69, 87, 89, 91, 93, and 95) were identified by mass spectrometry. Scandium-containing endohedral fullerenes were also repeatedly synthesized in negligibly small amounts. For example, Sc_2C_{66} was reported by Wang *et al.* [3]. The product was isolated in an amount of 2 mg from 800 g of a fullerene-containing soot, which corresponds to a total yield of 0.0025 at. %.

We have studied the possibility of obtaining endohedral fullerenes and heterofullerenes using a method realized in a setup described previously [4]. This reactor significantly differs from the conventional Krätschmer setup in that the synthesis is conducted at atmospheric pressure in an arc-generated carbon–helium plasma jet. The plasma jet length reaches about 75 cm at an arc current of 500 A. The temperature varies from 5000 K near the external electrode to 2000 K in the arc tail. Thus, the reactor allows particles of a working substance to stay for a sufficiently long time in the carbon plasma jet, so as to ensure complete atomization of the material. We have conducted the fullerene synthesis with introduction of Sc and B under these conditions.

The initial metallic powder of Sc_2O_3 was charged into a channel in the central electrode [4]. The fullerene-containing soot was treated with benzene in a Soxhlet apparatus, filtered, and evaporation dried. The quantitative content of metal in fullerene was determined using a special setup [5]. According to the data of elemental mass spectrometry and emission spectroscopy, the content of Sc in fullerene was 0.0016 at. %. Figure 1 shows fragments of the emission spectra displaying a Sc peak at 424.683 nm.

The synthesis of boron-containing fullerenes was performed by introducing a B_2O_3 powder into the carbon–helium plasma jet using a special device [6]. The emission spectra of the boron-containing soot and fullerene samples contained a characteristic boron line at 249.773 nm. The relative boron peak intensities in these samples were 183 and 121 units at a background intensity on the order of 40 units. According to the results of mass-spectroscopic measurements, which coincided with the emission spectroscopy data, the rel-

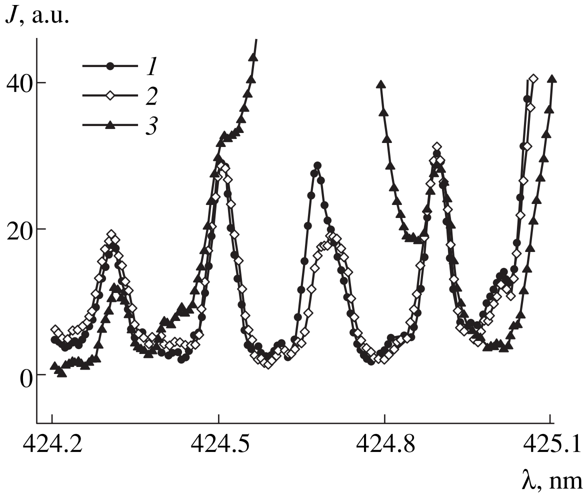

Fig. 1. Emission spectra of samples measured in an argon flow: (*1*) Sc-containing fullerene; (*2*) blank spectrum (discharge without sample introduction); (*3*) Sc-containing fullerene soot.

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ative amount of boron-containing fullerenes in the fullerene mixture exceeded 11%.

The benzene extract from a fullerene-containing soot was analyzed on an MI-1201 mass spectrometer modified for high-temperature measurements [7]. The sample was evaporated from a stainless-steel effusion cell and ionized by electron impact at an energy of 60–80 eV.

At temperatures below 515 K, the relatively low vapor pressure of $C_{59}B$ (as compared to that of C_{60}) and insufficiently high resolution of the instrument did not allow us to detect the peaks of ions with $m/e = 718$ and 719 corresponding to $C_{59}B$ molecules. However, the ion current intensity significantly increased with the temperature. This allowed the entrance slit width of the electrometric amplifier to be reduced so as to increase the instrument resolution and obtain a mass spectrum in the region of $m/e = 720$ (Fig. 2). The presence of ions with $m/e = 718$ and 719, together with a ratio of the ion currents characteristic of the boron isotope composition, is evidence for the presence of $C_{59}B$ molecules in the gas phase. This is additionally confirmed by the character of variation of the ratio of $C_{59}B^+$ ion currents with $m/e = 718–719$ and that with $m/e = 720–723$ corresponding to the carbon isotope composition in C_{60} molecules (a contribution of the boron-containing ions with $m/e \geq 720$ is very small). Inside each group, the ion current intensity ratio remains constant during the temperature variation (to within the experimental error), while consistently changing for the ions of various groups. The temperature variation of the relative intensity of $C_{59}B^+$ ($m/e = 719$) and C_{60}^+ ($m/e = 720$) ion currents is presented in the table and can be analytically described by the equation $\log\{I(C_{59}B^+)/I(C_{60}^+)\} = -(1.68 \pm 0.70)/T + (1.85 \pm 0.92)$.

In the region of masses corresponding to C_{70}, the ion peaks were resolved much worse than the peaks of $C_{59}B$ and C_{60}. Nevertheless, even distorted peaks are indicative of the presence of C_{70} and $C_{69}B$ molecules in the gas phase.

At a constant temperature of 790 K, the current of $C_{59}B^+$ ions decreases in intensity with time (relative to that of C_{60}^+) and eventually virtually complete disappears. This can be explained either by a decrease in the activity of $C_{59}B$ in a solid solution of this compound in C_{60} or by diffusion limitations of the $C_{59}B$ flow toward the sample surface. Distinguishing between the two factors requires additional investigation. However, we have determined the saturated vapor pressure and the parameters of sublimation for $C_{59}B$, assuming equal (unity) activities of $C_{59}B$ and C_{60}. For $a(C_{59}B) = a(C_{60})$, we can approximately take $I(C_{59}B^+)/I(C_{60}^+) \sim p(C_{59}B)/p(C_{60}) = p°(C_{59}B)/p°(C_{60})$. With an allowance for the known temperature dependence of the saturated vapor pressure of C_{60}, $\log\{p°(C_{60})\,[\mathrm{Pa}]\} = -(9.154 \pm 1.50)/T + (8.28 \pm 0.2)$ [7], this yields $\log\{p°(C_{59}B)\,[\mathrm{atm}]\} = -(10838 \pm 166)/T + (5.12 \pm 0.73)$, $\Delta_s H_T^\circ = 208 \pm 18$ kJ/mol, and $\Delta_s S_T^\circ = 98 \pm 18$ J/(mol K).

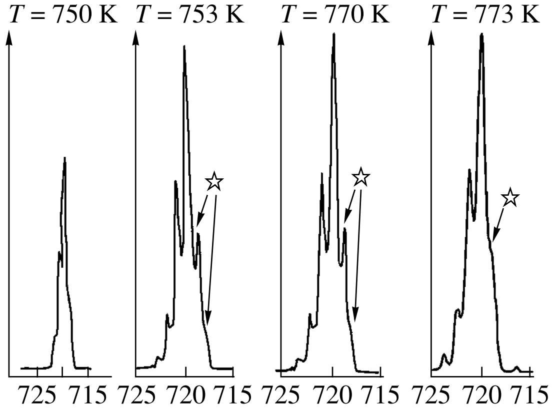

Fig. 2. Temperature variation of a fragment of the mass spectrum of a fullerene extract synthesized upon boron introduction. Stars indicate the peaks corresponding to $C_{59}B$ molecules.

The greater enthalpy of sublimation obtained for $C_{59}B$ as compared to that for C_{60} can be explained by the fact that the former molecular possesses a dipole moment and, hence, features a stronger intermolecular interaction.

Thus, we have synthesized scandium- and boron-containing fullerenes using a plasmachemical reactor operating at atmospheric pressure. The synthesized fullerenes were studied by emission spectroscopy and mass spectrometry. The results of these measurements confirmed the formation of scandium-containing fullerenes. The content of Sc in the product is very small, amounting to 0.0016 at. %. The formation of boron-doped fullerene was also confirmed. The relative content of this compound in the fullerene mixture exceeds 11%. Thus, the case with boron shows that het-

Temperature variation of the ratio of $C_{59}B^+$ and C_{60}^+ ion currents in the mass spectrum of a boron-doped fullerene

T, K	719	753	769	770	790	773	757
$\log\{I(C_{59}B^+)/I(C_{60}^+)\}$	0.495	0.377	0.238	0.279	0.299	0.418	0.408

erofullerenes can readily form in a carbon–helium plasma jet at atmospheric pressure.

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