

Intercalation of fullerite C₆₀ with Potassium: ¹³C and ³⁹K NMR data

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Intercalation of fullerite C₆₀ with alkaline metals is known to yield a series of stable and metastable compounds A_xC₆₀ (A = Na, K, Rb, Cs; x = 1-6) exhibiting different structural, magnetic, electrical properties. The properties of the compounds and phase transformations in the A-C₆₀ systems are of considerable interest.

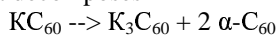
In this work, stable compounds in the K-C₆₀ system were studied using the NMR method. The choice of the method and the system was determined by two reasons: first, the NMR method was established to be a powerful tool for studying [C₆₀]fullerite intercalated with alkaline metals [1], and, secondly, earlier we have built the phase diagram of the binary K-C₆₀ system [2].

The samples of stoichiometric compositions K_xC₆₀ (x=1,3,4,5,6) were prepared using potassium in the form of metal (K) or metal hydride (KH). All operations with these substances were carried out in a glove box (residual oxygen content, 2 ppm, and water content, 1 ppm). The samples of K_xC₆₀ were synthesized by heating potassium and fullerite C₆₀ in quartz evacuated and sealed ampoules at 500-700 K for about 30 days. The ¹³C and ³⁹K spectra of each reaction mixture and the products formed after heating for 15 and 30 days were recorded

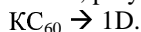
The ¹³C NMR spectra were taken at room temperature in two polarizing fields (B₀=4,7 T, 50,3 MHz, Bruker AC-200 and B₀ = 7,04 T, 75,4 MHz, Bruker MSL-300). One-pulse sequence was used to excite the C-13 spin system. The ³⁹K NMR spectra were registered at room temperature (7.04T, 13,99 MHz, Bruker MSL-300) using a quadro-echo sequence.

The signals in ¹³C and ³⁹K NMR spectra were identified using the literature data [1,3,4] and the phase diagram of the K-C₆₀ system [2].

Particular attention was paid to the composition of the samples of K₁C₆₀. This compound is thermodynamically stable at T>420 K, while at T<420 K, it decomposes



and, in addition, polymerizes



Several samples of K₁C₆₀ were obtained by cooling the reaction products with different rate from T>420 K to T<300 K. The phase composition of the samples was estimated from the ratio of the measured integral intensities of the peaks in ¹³C NMR spectrum, a set of stable and metastable phases being obtained, depending on the conditions of thermal treating.

The shifts of ³⁹K signals and their integral intensities in spectra of all samples indicated that the potassium atoms occupy in fullerite C₆₀ two sites

(octahedral and tetrahedral) with a constant occupancy ratio of 2 : 1.

We were succeeded in distinguishing chemical shifts of ¹³C assigned to free C₆₀ and to C₆₀ in a solid solution of potassium in fullerite C₆₀ (2 ppm).

The results of studies of other compounds in the K-C₆₀ system will be also presented in this report. Correlation between the structural properties of these compounds and dynamics of motion of ionized C₆₀ molecules and K atoms will be discussed.

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