

Low-temperature photoluminescence of C₆₀ single crystals intercalated with nitrogen molecules in the wide range of temperatures

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The optical properties of C₆₀ single crystals, intercalated with nitrogen molecules, were studied by the spectral-luminescence method at a temperature $T = 30$ K and excitation by the He–Ne laser ($E_{\text{exc}} = 1.96$ eV). Intercalation was carried out at a pressure of 30 atm in a temperature range of 200–550 °C. It was found that at sorption temperatures up to 400 °C, the bands of the low-temperature luminescence spectrum of the C₆₀–N₂ solutions are broadened without significant energy shift. As a rule, this situation is typical for the case of an increased contribution of the luminescence of “deep X-traps”. The concentration of such exciton emission centers is determined by the degree of occupation of the octahedral cavities of the fullerite fcc lattice by intercalated molecules. This indicates the formation of an equilibrium C₆₀–N₂ interstitial solution as a result of physisorption. At sorption temperatures above 400 °C, a significant shift of the luminescence spectrum towards low energies with a considerable inhomogeneous broadening of spectral bands was found for the first time. The shift and significant nonuniform broadening of the luminescence bands are explained by the emergence of a chemical interaction (chemisorption) of nitrogen with fullerene molecules, with the formation of a new nitrogen-containing substance in this case.

Keywords: fullerite C₆₀, N₂ intercalation, lattice parameters, photoluminescence, adsorption crossover.

Fullerite C₆₀ belongs to the class of molecular crystals [1, 2]. In these crystals the molecules are loosely bound to each other by van der Waals forces and retain to a large extent their individuality. Molecular crystals represent a wide range of compounds, the properties of which are of great interest, both from a scientific point of view and practical application.

The symmetry of the crystal structure of C₆₀ fullerite is determined by the rotational state of the molecules, which, depending on the temperature and the presence of impurities, can radically change. The orientationally disordered phase of fullerite C₆₀ in the temperature range above 260 K has lattice symmetry $Fm\bar{3}m$ with a characteristic weakly hindered spherical rotation of molecules. A decrease in temperature transforms the crystal structure into the $Pa\bar{3}$ symmetry with relatively free rotation of molecules only around their own third-order axes oriented along the $\langle 111 \rangle$ directions of the cubic cell. Complete freezing of molecular turns in the low-temperature region at $T < T_g = 90$ K leads to the formation of a kind of orientational glass [3, 4]. Fullerite contains structural interstitial voids of two types

with different sizes — octahedral (2.1 Å radius) and tetrahedral (1.1 Å radius) [2], which can be filled with interstitial impurities. Doping of fullerite with various atoms or molecules has a significant effect on the spectral-luminescent, structural, and thermodynamic characteristics of C₆₀ fullerite.

The luminescence of fullerite at low temperatures is determined by the efficiency of the transport of excitons to emission centers, as a rule, to structural defects and impurities, with the general name “deep X-traps” [5]. Localization of the Frenkel exciton on such inclusions strongly increases the probability of radiative transitions forbidden by symmetry for C₆₀ molecules in an ordered lattice [6]. As the temperature of C₆₀ fullerite intercalation by nitrogen molecules increases, the octahedral voids of the C₆₀ cubic lattice are gradually filled with a large dopant density gradient along the sample depth [7]. At a sorption temperature above 420 °C, the diffusion saturation mechanism is replaced by the formation of nitrogen-containing complexes [8], as a result of chemical interaction of nitrogen atoms with C₆₀ molecules.

In this article, we present the results of photoluminescence studies of the C_{60} - N_2 binary system at different temperatures of nitrogen sorption. The features of the spectral characteristics of the material under study for the case of physisorption of nitrogen, as well as for the transition to the mechanism of chemisorption, are established.

To study the spectral properties of fullerite intercalated with N_2 molecules, we used polycrystalline samples with a purity of at least 99.9 % with a crystallite size of about 0.5 μm , which were saturated with nitrogen at two different temperature regimes $T_s = 280^\circ\text{C}$ and $T_s = 450^\circ\text{C}$. The total intercalation time in the first and second modes was 150 and 200 h, respectively, at a gas pressure in the cell $P = 30$ atm. The control of the entry of the impurity N_2 molecule into the crystal lattice of fullerite was determined by the method of powder x-ray diffraction analysis at room temperature by the change in the lattice parameter a during saturation. A description of the process of saturation of C_{60} with N_2 molecules and x-ray diffraction data for the obtained samples are given in [8].

Figure 1 shows the change in the parameter a of the studied samples of C_{60} on the saturation temperature with gaseous N_2 on the base of experimentally obtained data [8]. A characteristic break of the change in the lattice parameter a at a temperature of $T_s = 450^\circ\text{C}$ indicates a change in the sorption mechanism.

The photoluminescence (PL) of C_{60} crystals at a temperature of 30 K was recorded “for reflection” in the spectral region 1.2–1.85 eV (1033–670 nm) with a spectral resolution of 2 nm, in the photon counting mode upon excitation of an He–Ne laser with radiation energy $E_{\text{exc}} = 1.96$ eV (632.8 nm) and power density $W \leq 1$ mW/mm². The luminescence measurement technique, experimental setup, and analytical processing of experimental results are presented in [6].

Figure 2 illustrates the photoluminescence spectra of polycrystal C_{60} samples at a temperature of 30 K, corrected

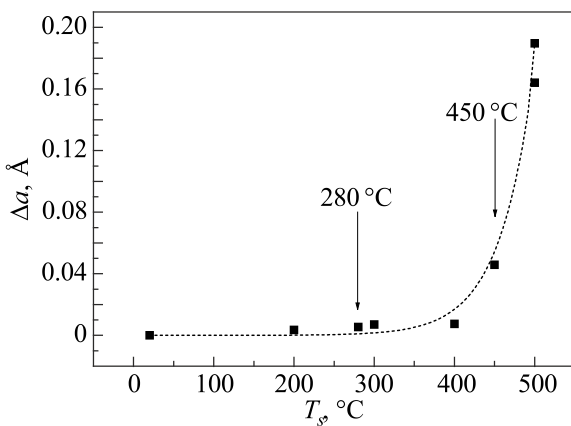


Fig. 1. The change in the parameter a of the studied samples of C_{60} on the saturation temperature T_s with gaseous N_2 at a pressure of 30 atm on the base of experimentally obtained data [8].

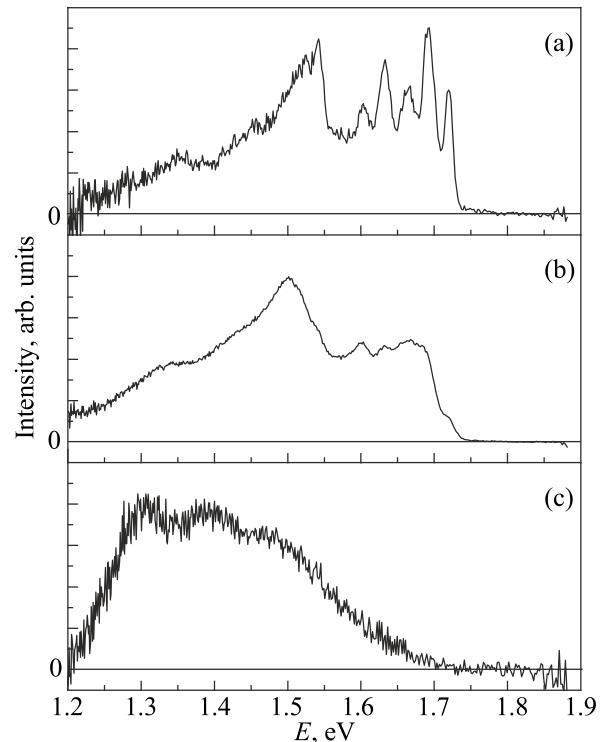


Fig. 2. The photoluminescence spectra of a polycrystal C_{60} samples at 30 K: (a) pure fullerite; (b) C_{60} saturated with molecular nitrogen at a temperature of 280°C and (c) saturated at a temperature of 450°C . The spectra were normalized to their integral intensity and corrected for the spectral sensitivity of the setup.

for the spectral sensitivity of the setup and normalized to their integral intensity at $T = 30$ K: (a) pure fullerite, (b) C_{60} saturated with molecular nitrogen at a temperature of 280°C , and (c) saturated at a temperature of 450°C . The main contribution to the luminescence of the C_{60} - N_2 solution in the diffusion mechanism of sorption is made by the radiation of a mobile exciton localized on “deep X-traps”. The intensity of such radiation depends on the concentration of intermolecular voids in the fullerite lattice filled with an intercalator. The significant inhomogeneous broadening of the spectral bands [Fig. 2(b)] indicates a significant filling of the octahedral voids of fullerite, which at a relatively weak change in the matrix lattice parameter a [8] indicates the presence of a strong gradient of the N_2 impurity distribution over the depth of C_{60} crystals. The absence of an energy shift of the characteristic spectral photoluminescence bands indicates an exclusive diffusion mechanism of sorption in this saturation mode.

When comparing the spectra of pure C_{60} and fullerite extremely saturated with nitrogen at two different temperatures (Fig. 2), the stepwise nature of changes in the photoluminescent properties with an increase in the intercalation temperature becomes obvious. The inhomogeneous broadening of the luminescence bands at $T_s = 280^\circ\text{C}$ [Fig. 2(b)] is replaced by a radical rearrangement of the spectrum with a strong shift to the low-energy region at $T_s = 450^\circ\text{C}$

[Fig. 2(c)] and a noticeable decrease in the radiation intensity. Joint analysis of spectral-luminescent and structural data [8] (including vacuum degassing) leaves no doubt about the presence of a sorption crossover. An increase in the saturation temperature above 420 °C for the C₆₀-N₂ system leads to a change in the diffusion mechanism of sorption to the chemical interaction of the intercalant with matrix molecules and, as a result, to the formation of a new nitrogen-containing substance based on C₆₀.

Thus, in this article, we have show a significant change in the optical characteristics for the C₆₀-N₂ binary system with a change in the sorption mechanism (adsorption crossover — transition from physisorption to chemisorption) for the first time. A slight change in the matrix lattice parameter and broadening of the C₆₀ luminescence spectrum bands characteristic of physisorption without an energy shift are observed in the sorption region up to 400–420 °C. This indicates that the octahedral cavities in C₆₀ crystallites are filled with nitrogen molecules with the formation of an equilibrium interstitial solution. A strong change in the spectral luminescence characteristics of the C₆₀-N₂ system was established at sorption temperatures above 420 °C. A shift of the luminescence spectrum towards low energies is observed. The shift and significant nonuniform broadening of the luminescence bands observed in the second region of saturation temperatures $T_s > 420$ °C are due to chemical sorption processes. In this case, nitriding of C₆₀ molecules occurs and a new nitrogen-containing substance is formed.

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Низькотемпературна фотолюмінесценція монокристалів C₆₀, які інтеркальовані молекулами азоту у широкому інтервалі температур

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Оптичні властивості монокристалів C₆₀, які інтеркальовані молекулами азоту, досліджено спектральним люмінесцентним методом при температурі $T = 30$ К та збудженні He-Ne лазером ($E_{\text{exc}} = 1.96$ eV). Інтеркаляція здійснювалася під тиском 30 атм у температурному інтервалі 200–550 °C. Встановлено, що при температурах сорбції до 400 °C відбувається розширення смуг спектру низькотемпературної люмінесценції розчинів C₆₀-N₂ без зміщення по енергії. Зазвичай така ситуація характерна для випадку зростання внеску люмінесценції «глибоких X-пасток». Концентрація таких емісійних центрів екситонів визначається мірою заповнення октаедричних порожнин ГЦК ґратки фулерита молекулами інтеркалянта. Це свідчить про утворення рівноважного розчину впровадження C₆₀-N₂ завдяки фізсорбції. При температурах сорбції вище 400 °C вперше виявлено істотне зміщення спектру люмінесценції в область низьких енергій зі значним неоднорідним розширенням спектральних смуг. Зміщення та значне неоднорідне розширення спектральних смуг люмінесценції пояснено появою хімічної взаємодії (хемосорбції) азоту з молекулами фулерену з утворенням у цьому випадку нової азотовмісної речовини.

Ключеві слова: фулерит C₆₀, інтеркаляція N₂, параметри ґратки, фотолюмінесценція, адсорбційний кросовер.