1. INTRODUCTION

Since the early 1990s, carbon nanotubes, both single-walled and containing two or more carbon walls, have become the objects of comprehensive experimental and theoretical investigations [1–5]. Of special scientific and practical interest are properties of the composites containing, in addition to nanotubes, other components that can surround the nanotube and fill its internal channel, which, as a rule, leads to a modification of the properties of nanostructured phases making up the composite. In particular, the structural, transport, and other characteristics of inorganic ionic solid phases embedded inside carbon nanotubes can significantly differ from those of the bulk phase [6–10]. This has opened up possibilities for the development of nanocomposite materials with variable and controllable properties.

Fluorides of Group II and IV metals in the oxidation state of +2 (CaF_2, SrF_2, BaF_2, SnF_2, PbF_2) are known as superionic conductors with a high fluorine ion conductivity over a wide temperature range below the melting point. Alkaline-earth metal fluorides exhibit a significant ion conductivity only at high temperatures (the superionic transition identified by a maximum in the heat capacity during heating is observed in CaF_2 and SrF_2 at temperatures of 1370–1380 K and in BaF_2 at 1245 K; the electrical conductivity in the region of the transition amounts to a few tenths of Ω^{-1} cm^{-1} [11], which corresponds to the diffusion coefficient of fluorine ions of the order of 10^{-9} m^2/s), whereas the isostructural (fluorite-like) β-modification of lead(II) fluoride undergoes a transition to the superionic state already at 710 K (the melting point of β-PbF_2 is 1128 K) [12, 13]. A possible explanation for these observations can be provided by the effects associated with a high polarizability of lead ions [14]. Tin(II) fluoride substantially differs from the aforementioned compounds by a number of characteristics. It is a relatively low-melting material (the melting point is 488 K), which in the solid state exists in the form of three polymorphic modifications (α-, β-, and γ-SnF_2 belonging to the monoclinic, orthorhombic, and tetragonal crystal systems, respectively; during heating, there occurs a transition α → γ at 423 K; during cooling, the γ phase transforms into the β phase at 339 K); at low temperatures, the conductivity of SnF_2 (of the order of 10^{-4} Ω^{-1} cm^{-1} when the transition temperature is approached) is mainly caused by the migration of anions, but above 440 K, the electronic component dominates—tin difluoride behaves as an n-type semiconductor [15–23]. A number of SnF_2-based mixed fluorides are anion-conducting solid electrolytes [22]; in particular, high fluorine ion conductivity at sufficiently low temperatures (even at 450–470 K, it is of the order of 10^{-1} Ω^{-1} cm^{-1}) is observed in lead(II) tetrafluorostannate(II) PbSnF_4.
The above features of SnF₂ and mixed fluorides based on SnF₂ were probably, reflect a specific character of chemical bonding in these compounds: apart from the high polarizability of ions, divalent tin tends to form Sn—F covalent bonds [22, 28].

For a number of inorganic halides, composites—products of the incorporation of the corresponding substance into internal channels of carbon nanotubes—were synthesized, and their crystal-chemical properties, electronic characteristics reflecting the interaction of a filler with the nanotube, and thermal stability were studied experimentally [7–10, 29–31]. Recently, inside single-walled carbon nanotubes (SWCNTs), nanostructures (one-dimensional crystals) of SnF₂ (SnF₂@SWCNT) were produced in [32–34]. The crystal-chemical analysis of SnF₂@SWCNT [34] was used to refine the understanding of the structure of tin(II) fluoride.

At the same time, experimental data on the mobility of ions in inorganic ionic phases within carbon nanotubes are still clearly lacking.

An additional important source of information about the properties of such systems can be computer simulation, including the classical “atomistic” molecular dynamics (MD) [35–41]. In our previous publications [42–44], we presented the results of the molecular dynamics simulation of nanostructures of silver iodide, silver bromide, and solid solutions AgIₓBr1–x inside SWCNTs. It was revealed that, in these model systems, ordered nanotubular structures AgI₁₋ₓBrₓ are formed in sufficiently narrow SWCNTs, while “nanowires” with a less regular ionic arrangement are formed in broader SWCNTs. In all cases, in the temperature range approximately 150 K below the melting point, significant silver ion conductivity was observed against the background of low-mobile halogen anions in the filled internal channel of the nanotube. At the same time, a comparison of the results of the simulation with available experimental data (high-resolution transmission electron microscopy) indicates the necessity of improving the model potentials.

In this work, we made an attempt to investigate the SnF₂@SWCNT system by the MD method using the model potentials available in the literature. The purpose of our work was, in particular, to elucidate the possibility of high fluorine ion conductivity in combination with a relatively stable sublattice of tin ions in model systems at temperatures below the melting point. Taking into account the above characteristics of the interionic interaction in tin(II) fluoride, it could be assumed that the models based on the “rigid-ion” approximation will most likely be of little use for the description of the properties of SnF₂ and can be mainly of illustrative value. In this respect, special attention was paid to the simulation taking into account the ion polarization.

2. DESCRIPTION OF THE MODELS AND SIMULATION TECHNIQUE

As a first rough approximation for the simulation of SnF₂@SWCNT, we used the approximate pairwise additive UFF (universal force field) potential developed on the basis of calculations of the properties of organic and organometallic compounds [45] (which was also applied to complexes of some metals with organic ligands [46]). The interaction of atoms or ions in the simulated system in this case was described by the sum of the Coulomb and Lennard-Jones potentials

\[ U_{ij} = \frac{Z_i Z_j e^2}{r_{ij}} + 4\varepsilon_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^6. \]  

In addition, the expression for the energy of the model system includes the energies of bending and stretching vibrations of the SWCNT.

The values of the UFF parameters were taken from [45], except for the effective charges of the tin and fluorine ions, which were obtained from the quantum-chemical calculations [47] and had the following values: \( Z_{\text{Sn}} = +1.77 \) and \( Z_{\text{F}} = -0.885 \).

The second model used in this work is based on the potential proposed by Castiglione et al. [27] for the simulation of PbSnF₄. This model approximately accounts for the effects associated with the polarization of the ions and describes the Sn—Sn, Sn—F, and F—F interactions in the form

\[ U_{ij}(r_{ij}) = \frac{B_i \exp(-a_i r_{ij})}{r_{ij}} + B_j \exp(-a_j r_{ij}') + \sum_{n=6,8} \frac{C_{n,ij}}{r_{ij}^n} f_{ij}^n(r_{ij})^n, \]

\[ f_{ij}(r) = 1 - c_{ij} \sum_{k=0}^{4} \frac{(b_{ij} r)^k}{k!} \exp(-b_{ij} r). \]

The model parameters were taken from [27]. The Sn—C and F—C interactions were described using the Lennard-Jones potential with the UFF parameters, and the energy of the carbon nanotube itself (as in [42–44]) was calculated using the Tersoff model potential [48].

A constraining potential was imposed on the system in the form of a repulsive cylindrical wall around the SWCNT and planar walls at the ends of the nanotube.

The initial configuration of the SnF₂@SWCNT structure was constructed by placing tin and fluorine ions inside the SWCNT in a random way, but with the following restrictions: (1) the distance between two ions should not exceed 2 Å; (2) the distance between the ion and the carbon atom should not exceed 3 Å; (3) the total number of introduced ions should not