

Molecular Dynamics Simulations of the Formation Processes and Luminescence Properties of Zn-ZnO Core-Shell Nanostructures

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We carried out molecular dynamics (MD) simulations of the oxidation of zinc nanoclusters to investigate the process of the formation of Zn-ZnO "core-shell" nanoclusters. In the present work it is being shown that the structure, shape and oxide layer thickness of the obtained particles directly depend on the initial oxygen density and initial temperature of the system. An increase of initial oxygen density the oxide layer thickness of obtained nanoparticles increase to a certain limit. During the analysis it was found, that created clusters mainly preserved their structure of core, but structure of shell commonly was amorphous. Also, we had studied the luminescence properties of experimentally created nanostructures. It was observed increase in quantum efficiency of luminescence.

Keywords: Nanopowders, Core-Shell structure, Metal oxides, Photoluminescence, Molecular dynamics.

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1. INTRODUCTION

Nowadays we can observe especially active processes of researching and studying the metal oxide nanomaterials that have a large number of original physical and chemical properties. Nanoparticles are prominent in usage on different fields of technical use, among them sensors take a special place [1, 2]. Zinc Oxide (ZnO) plays vital role in building different kind of sensors. It is a very interesting material with a wide range of technical attachments. It can serve as a working element in electronic devices, solar cells and gas sensor systems [3-5].

One of the simplest and most popular methods of obtaining nanoparticles is the gas phase method of evaporation of a solid-metal target material in the atmosphere of reactive gas followed by condensation on the substrate surface [6-8]. Pulsed laser ablation is used for heating the material with subsequent evaporation. We suggest a method of the synthesis of metal oxide nanopowders by pulsed laser evaporation of a metal target in a chemically active oxygen environment [9]. The laser impulse heats the material of the metal pellet to a high temperature. Thus, atoms of the pellet evaporate into the system with a working chemical-active background gas. Such a mixture of gases contributes reducing of the kinetic energy of evaporated atoms and their chemical interaction, which leads the formation of nanoclusters. During the process of laser reactive synthesis under some conditions there is a near-surface oxidation of nanoparticles that detached from the target's surface in the form of droplets or formed in a vapor-phase torch from metallic target atoms. This allows us to create complex materials, such as "core-shell" nanopowders. By carefully selecting laser radiation parameters and the pressure of background gas, we have the ability to control the structure, size and thickness of the oxide layer of the obtained structures.

It is known that the properties of nanoparticles are determined by their structure, shape and size, which, in

turn, is the result of the growth process of nanoparticles [10]. Experimental study of mechanisms of the formation of nanoparticles is a technically complex and time-consuming task due to the fastness of the processes and the small size of these objects. In the conditions of the experimental gas phase synthesis, is, somewhat, complicated to study in detail the influence of the basic parameters of synthesis on the physico-chemical and structural properties, as well as the external form of the resulting particles. Therefore, computer simulation is an alternative and promising way to study the mechanisms of the formation of nanobjects. Using computer simulation methods allows us to study the processes of growth and synthesis of nanoparticles in condensation from the gas phase in detail. [11]. In this work we had studied the processes of oxidation of Zn nanoparticles in the oxygen environment by molecular dynamics method. Also, we had thoroughly studied the luminescent properties of experimentally created nanostructures.

2. MODEL AND METHOD

We simulated the process of the formation of Zn-ZnO nanoparticles using molecular dynamics method. This computer simulation method is determined by numerically solving Newton's equations of motion for each atom of the system under given initial conditions. In the classical molecular dynamics, the method of the interaction between atoms is described by empirical force fields, and the particles, that interact with each other are represented as point masses [12, 13]. A crucial step in establishing the correct model is to choose the correct interatomic potential for atoms of the system. By analyzing the nature of the formation of such nanostructures and referring to sources about the interatomic potentials, we have chosen the Reactive Force Field (ReaxFF) potential [14, 15]. This potential is designed for a wide range of chemical compounds, including for ZnO and already had been used by us in previous studies about the simulation of processes

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of the formation of ZnO nanoparticles in chemically active environment [16].

ReaxFF is an empirical potential that derived from quantum-mechanical calculations. The bond order is directly calculated from an interatomic distance and updated every iteration for all bonded interactions, including covalent bonds, valence, and torsion angles. In addition, the ReaxFF describes non-bonded van der Waals and Coulomb interactions. Such interactions are calculated for all pairs of atoms, and, by incorporating a shielding term, extremely close-range interactions can be modified. Polarization effects also are considered by using a geometry-dependent charge distribution derived from an electronegativity equalization method [17].

For this type of problem we used software package Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS), developed by a scientific group from the National Laboratory of Sandia. Calculations were performed by us on a computing cluster of the Institute of Applied Problems of Mechanics and Mathematics, which is based on four Intel Xeon multi-core processors under operating system Linux ROCKS.

The initial conditions of the simulation of the oxidation process of Zn nanoparticles were six configurations. We have been changing the size of the initial cluster Zn (2-4 nm), also, the oxygen concentration (2.6×10^{19} , 6×10^{19} , 1.18×10^{20} atoms/cm³) in the investigated volume (8000 nm³) and the temperature of the system (300, 600 K). The size of the cells for these configurations were the same ($200 \times 200 \times 200 \text{ \AA}^3$) and it was done in order to set different initial gas concentrations. In order to avoid the premature union of atoms in the initial stages of simulation, the atoms were located in the nodes of the cubic lattice and the distance between the atoms was set to be greater than the cut-off of the potential, and therefore the gas atoms were not connected with each other at the initial moment of time.

The directions of the initial velocities of oxygen atoms were chosen randomly, the values of the initial velocities were set according to the temperature of the system. The temperature in the investigated volume was maintained at a fixed two values ($T = 300, 600 \text{ K}$). The key point of simulation is the connection of the system with the thermostat to maintain a specific temperature of the system. Since a significant amount of energy was released in the process of oxidation of nanoclusters, such a connection is necessary in order to avoid additional increases in temperature. In real experiments, this connection is provided by inert gas. In our computer simulation, temperature control was achieved by using the Berendsen thermostat method [18, 19]. This method is widely used to simulate the molecular dynamics of the systems with a large number of degrees of freedom. To maintain temperature, the system is connected to an external thermostat with a fixed temperature. The speeds are calibrated at each step in such way, that the change in temperature velocity is proportional to the temperature difference of the system and thermostat.

During simulation, the snapshots of the system was stored every 0.5 ps. These snapshots, in addition to visual observation, were, also, used to analyze the shape, size, structure and thickness of the oxide layer of newly formed nanoparticles. To analyze the internal structure

of clusters, we used the Common Neighbor Analysis (CNA) method [20].

3. RESULTS AND DISCUSSION

“Core-shell” Zn-ZnO nanoclusters were investigated objects in our work. During the study, it was established that the structure, thickness of the oxide layer and the shape of the nanoparticles depends on the initial conditions of formation, namely, the initial concentration of gas and temperature of the system.

The oxidation process for different systems, with different initial conditions, took place differently. Figure 1 shows the image of the system at the initial moments of time for various configurations. Gas concentrations were chosen relatively large in order to be able to simulate the oxidation process of nanoparticles for a relatively small given simulation time (2 ns). In order to demonstrate how the temperature influences on thickness of the oxide layer of nanoparticles, we conducted MD simulations at two different initial temperatures (300 and 600 K). For nanoclusters with a diameter 2 nm under these initial conditions, the separation between the nucleus and the oxide shell was not observed. Oxygen atoms were diffused completely into the cluster volume and ZnO nanoclusters were formed.

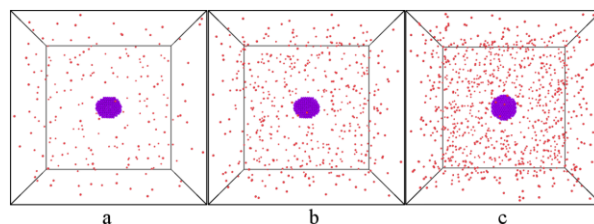


Fig. 1 – Snapshots of the system at the initial moments of time for different initial concentration of O atoms: (a) 2.6×10^{19} (b) 6×10^{19} (c) 1.18×10^{20} atoms/cm³

Figure 2 shows the snapshots of the cross sections of nanoobjects with diameter 4 nm at the end point of time. From the figures it is seen that as the temperature rises, there is no clear distinction between the oxide film and the nucleus of nanocluster and ZnO nanoclusters are formed. This is due to the fact that nanoclusters with such sizes at a temperature 600 K begin to melt, the structure became amorphous, for oxygen atoms it was much more easier to penetrate deep into the nanoparticle. Also, at Figure 2 we can observe changing on the thickness of the shell of finite nanoclusters within changing gas pressure. It is visually seen that with increasing values of the initial gas pressure there is an increase of the thickness of the oxide film, and the structure of the film differs from the structure of the nucleus.

The dependence of the number of oxygen atoms on the surface of Zn nanocluster with time for nanoclusters with a diameter 4 nm and with 300 K temperature is shown in Figure 3a, and with 600 K temperature in Figure 3b. From these dependences it follows that at room temperature, the oxide shell reaches the peak of the thickness, and at $T = 600 \text{ K}$ the film grows until the cluster completely oxidizes and until ZnO nanoparticle is not

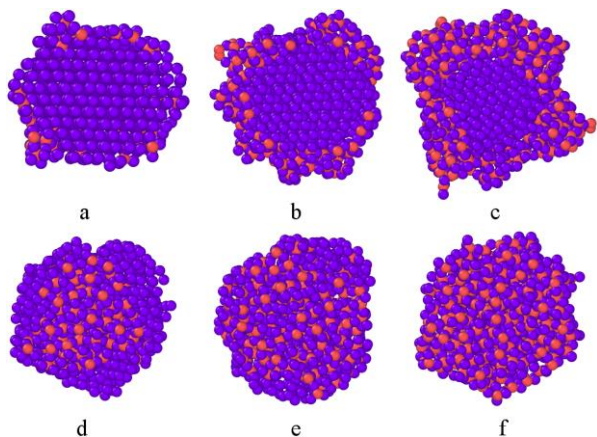


Fig. 2 – Snapshots of the cross sections of Zn-ZnO nanoparticles ($d = 4$ nm) at $t = 2$ ns for different initial concentration of O atoms and temperature:

(a) $n = 2.6 \times 10^{19}$ atoms/cm³, $T = 300$ K; (b) $n = 6 \times 10^{19}$ atoms/cm³, $T = 300$ K; (c) $n = 1.18 \times 10^{20}$ atoms/cm³, $T = 300$ K; (d) $n = 2.6 \times 10^{19}$ atoms/cm³, $T = 600$ K; (e) $n = 6 \times 10^{19}$ atoms/cm³, $T = 600$ K; (f) $n = 1.18 \times 10^{20}$ atoms/cm³, $T = 600$ K

formed. As was said above, this is due to the fact that for a given size of nanoclusters the temperature of 600 K is sufficient to melt the nanoparticle.

Figure 4 shows the functions of radial distribution for nanoparticles under different initial conditions. This function allows us to determine the probability that two atoms are located at a certain distance from each other [21]. And depending on the placement of atoms, we can determine which nanoclusters are amorphous and which are crystalline. The peaks of curves of radial distribution function correspond for interatomic distances. The black color is marked curves at the initial moments of time, and in red at the final moments of time. It is evident that at the initial moments of time one of the greatest peaks is clearly expressed. This is due to the fact that

the nanocluster consists only of Zn atoms. With an increase of the initial gas concentration, there is a decrease of that initial peak and an increase in peak in the vicinity of 2 Å. This is due to the fact that the oxygen atoms penetrate inside the pure Zn nanoclusters and the probability of finding O atoms in that nanoclusters increases.

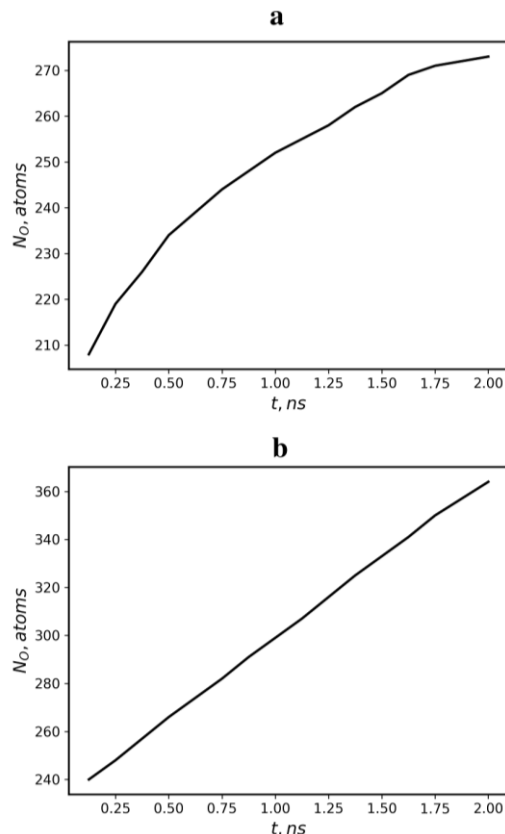


Fig. 3 – Dependence of the number of oxygen atoms on the surface of Zn nanocluster with time for different initial temperature: (a) 300 (b) 600 K

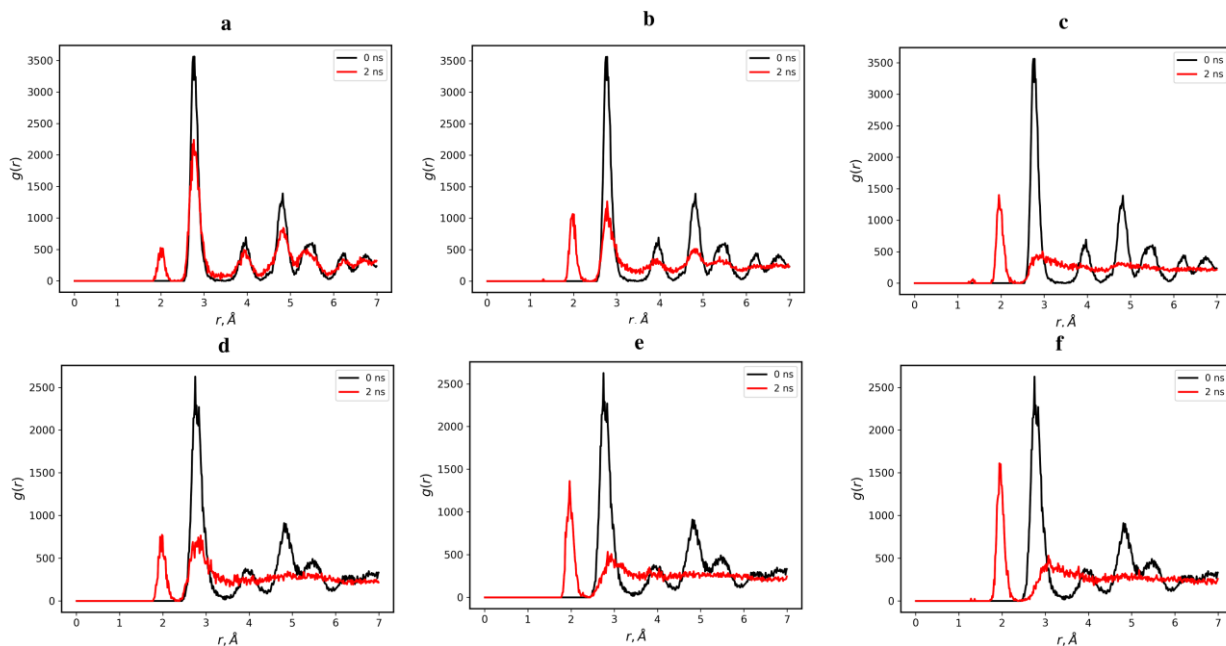


Fig. 4 – Radial distribution functions of nanoparticles under different initial conditions:

(a) $n = 2.6 \times 10^{19}$ atoms/cm³, $T = 300$ K; (b) $n = 6 \times 10^{19}$ atoms/cm³, $T = 300$ K; (c) $n = 1.18 \times 10^{20}$ atoms/cm³, $T = 300$ K; (d) $n = 2.6 \times 10^{19}$ atoms/cm³, $T = 600$ K; (e) $n = 6 \times 10^{19}$ atoms/cm³, $T = 600$ K; (f) $n = 1.18 \times 10^{20}$ atoms/cm³, $T = 600$ K

If we take look at the change of $g(r)$ function from temperature, then it can be seen that the initial peak corresponding to a pure Zn nanoclusters almost disappears at 600 K temperature, and, consequently, there is no separation between the nucleus and the oxide layer, the O atoms penetrate inside the entire volume of the Zn nanocluster. That is, the thickness of the shell of the “core-shell” structure depends on the distance to the target (temperature on different areas) in the laser evaporation.

Also we had analyzed the change in the structure of Zn-ZnO nanoclusters with a change in temperature and gas pressure. During the analysis, it was discovered that for a 300 K temperature, nanoclusters retain the structure of the nucleus, but the shell structure was almost always amorphous, and for the temperature 600 K the cluster structure is mostly amorphous, there is no separation between the core and the shell. It is clear that the percentage of amorphous structure grows with the growth of gas concentration, due to the growth of the oxide shell.

In the experimental created heterostructures such as “core-shell” [22] an increase in quantum efficiency of luminescence is being detected. For such systems, the processes of chemisorption of gas components determine the height of the energy barrier for current carriers at the boundary of a nanocrystalline system, which leads to increased gas sensitivity (Figure 5).

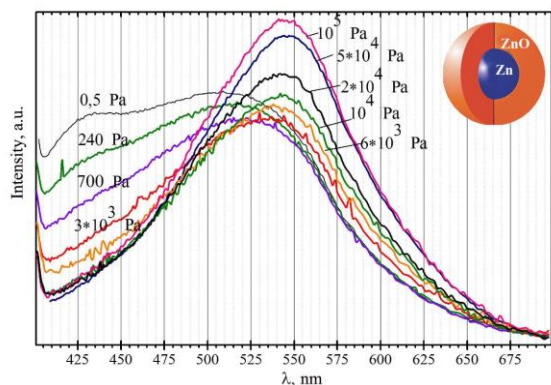


Fig. 5 – Photoluminescence spectra of “core-shell” Zn-ZnO nanobjects under different gas pressures

The electron structure of the heterojunction here is

Моделювання процесів формування методом молекулярної динаміки та люмінесцентні властивості наноструктур Zn-ZnO типу ядро-оболонка

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Нами було проведено молекулярно-динамічне (МД) моделювання окислення нанокластерів цинку для дослідження процесу формування Zn-ZnO “ядро-оболонка” наночастинок. В даній роботі показано, що структура, форма та товщина оксидного шару отриманих частинок безпосередньо залежить від початкової концентрації кисню та початкової температури системи. Встановлено що при збільшенні початкової концентрації кисню товщина оксидного шару збільшується до певної межі. Під час аналізу було встановлено, що утворені нанокластери в основному зберігали свою структуру ядра, а в свою чергу структура оболонки зазвичай була аморфною. Також ми вивчали люмінесцентні властивості експериментально створених нами наноструктур. Було відзначено збільшення квантової ефективності люмінесценції.

Ключові слова: Нанопорошки, Структура ядро-оболонка, Металооксиди, Фотолюмінесценція, Молекулярна динаміка.

such, that the electron and the hole are energetically favorable to be found in different parts of the nanogranule, which leads to appearance of uncompensated charge regions, and, accordingly, to appearance the electric field in the center of the nanoparticle. Because of the separation of charge carriers, there is a change in the spectral position of electronic transitions. Through the modifying in “core-shell” structure the core size and shell thickness, we can control the charge separation process and modify the spectral position of the optical transition. In return, the inconsistency of the lattice parameters of the “core-shell” heterocontact leads to mechanical deformation (compression of the ZnO shell), since, the lattice parameter of ZnO ($a = 0.33295$ nm, $c = 0.52069$ nm) [23], which also affects the electronic structure of the system.

4. CONCLUSIONS

In this research, we carried out molecular dynamics simulations of the oxidation of zinc nanoclusters to investigate the process of the formation of Zn-ZnO “core-shell” nanostructures. Also, we had studied the luminescent properties of experimentally created Zn-ZnO nanostructures. We performed MD simulations with three initial temperatures, three different initial oxygen density and two initial sizes of Zn nanoclusters. Depending on that it is possible to obtain different by structure, oxide layer thickness and shape Zn-ZnO “core-shell” nanoparticles. In the present work it is shown that the structure, shape and oxide layer thickness of the obtained particles directly depends on the initial oxygen density and initial temperature of the system. At increasing of initial oxygen density the oxide layer thickness of obtained nanoparticles increase to a certain limit. During the analysis it was found, that created clusters mainly preserved their structure of core, but structure of shell commonly was amorphous. From experimental study of photoluminescence of “core-shell” nanostructures it was observed increase in quantum efficiency of luminescence. Through the modifying in “core-shell” structure the core size and shell thickness, we can control the charge separation process and modify the spectral position of the optical transition. The results are in good agreement with experimental results and earlier molecular dynamics simulations.

Моделирование процессов формирования методом молекулярной динамики и люминесцентные свойства наноструктур Zn-ZnO типа ядро-оболочка

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Нами было проведено молекулярно-динамическое (МД) моделирование окисления нанокластеров цинка для исследования процесса формирования Zn-ZnO "ядро-оболочка" наночастиц. В данной работе показано, что структура, форма и толщина оксидного слоя полученных частиц напрямую зависит от начальной концентрации кислорода и начальной температуры системы. Установлено, что при увеличении начальной концентрации кислорода толщина окислительного слоя увеличивается до определенного предела. При анализе было установлено, что образованные нанокластеры в основном сохраняли свою структуру ядра, а в свою очередь структура оболочки обычно была аморфной. Также мы изучали люминесцентные свойства экспериментально созданных нами наноструктур. Было отмечено увеличение квантовой эффективности люминесценции.

Ключевые слова: Нанопорошки, Структура ядро-оболочка, Металлооксиды, Фотолюминесценция, Молекулярная динамика.

REFERENCES

1. I.B. Olenych, O.I. Aksimentyeva, L.S. Monastyrskii, U.Yu. Horbenko, L.I. Yarytska, *Nanoscale Res. Lett.* **10**, 187 (2015).
2. G. Fedorenko, L. Oleksenko, N. Maksymovych, G. Skolyar, O. Ripko, *Nanoscale Res. Lett.* **12**, 329 (2017).
3. V.M. Zhyrovetsky, D.I. Popovych, S.S. Savka, A.S. Serednytski, *Nanoscale Res. Lett.* **12**, 132 (2017).
4. Ya.V. Bobitski, R.V. Bovhyra, D.I. Popovych, S.S. Savka, A.S. Serednytski, V.N. Shevchuk, Yu.I. Venhryn, *J. Nano-Electron. Phys.* **9** No 5, 05008 (2017).
5. M. Madel, J. Jakob, F. Huber, B. Neuschl, S. Bauer, Y. Xie, I. Tischer, K. Thonke, *phys. status solidi a* **212** No 8, 1810 (2015).
6. K.V. Anikin, N.N. Melnik, A.V. Simakin, G.A. Shafeev, V.V. Voronov, A.G. Vitukhnovsky, *Chem. Phys. Lett.* **366**, 357 (2002).
7. B.N. Chichkov, C. Momma, S. Nolte, F. von Alvensleben, A. Tünnermann, *Appl. Phys. A* **63**, 109 (1996).
8. D.K. Pallotti, X. Ni, R. Fittipaldi, X. Wang, S. Lettieri, A. Vecchione, S. Amoruso, *Appl. Phys. B* **119**, 445 (2015).
9. Y. Bobitski, B. Kotlyarchuk, D. Popovych, V. Savchuk, *Proc. SPIE* **4425** (2001).
10. F. Zhiyong, G. Lu Jia, *J. Nanosci. Nanotechnol.* **5**, 1561 (2005).
11. R. Bovhyra, D. Popovych, O. Bovgyra, A. Serednytski, *Nanoscale Res. Lett.* **12**, 76 (2017).
12. D. Frenkel, B. Smit, *Understanding Molecular Simulation. From Algorithms to Applications* (San Diego: Academic Press: 2002).
13. D.C. Rapaport, *The Art of Molecular Dynamics Simulation* (Cambridge: Cambridge University Press 2004).
14. D. Raymand, A.C.T. van Duin, M. Baudin, K. Hermansson, *Surf. Sci.* **602**, 1020 (2008).
15. A.C.T. van Duin, O. Verneris, Y.-K. Shin, *Int. J. Energ. Mater. Chem. Propul.* **12**, 95 (2013).
16. S.S. Savka, D.I. Popovych, A.S. Serednytski, *Springer Proc. Phys.* **195**, 145 (2016).
17. W.J. Mortier, S.K. Ghosh, S. Shankar, *J. Am. Chem. Soc.* **108**, 4315 (1986).
18. P.H. Hunenberger, *Adv. Polymer. Sci.* **173**, 105 (2005).
19. H.J.C. Berendsen, J.P.M. Postma, W.F. van Gunsteren, A. DiNola, J.R. Haak, *J. Chem. Phys.* **81**, 3684 (1984).
20. J.D. Honeycutt, H.C. Andersen, *J. Phys. Chem.* **91**, 4950 (1987).
21. F. Daan, S. Berend, *Understanding molecular simulation from algorithms to applications (2nd ed.)* (San Diego: Academic Press: 2002).
22. V. Zhyrovetsky, B. Kovalyuk, V. Mocharskyi, Y. Nikiforov, V. Onisimchuk, D. Popovych, A. Serednytski, *phys. status solidi c* **10**, 1288 (2013).
23. D.R. Lide (Ed.), *CRC Handbook of Chemistry and Physics, 73rd Edition* (New York: CRC Press: 1992).