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Modeling the interaction of PbSe nanoparticles

P V Zakharov^{1,5}, I S Lutsenko², A V Markidonov³ and A I Cherednichenko⁴

¹Peter the Great St. Petersburg Polytechnic University, 29 Politekhnicheskaya St., 195251, St. Petersburg, Russia

²Polzunov Altai State Technical University, ave. Lenina 46, Barnaul 656038, Russian Federation

³Novokuznetsk Branch-Institute of Kemerovo State University, 23 Tsiolkovsky St., 654041, Novokuznetsk, Russia

⁴Shukshin Altai State University for Humanities and Pedagogy, 53 Vladimir Korolenko St., 659333, Biysk, Russia

⁵E-mail: zakharovpvl@rambler.ru

Abstract. In this work, the interaction of two PbSe nanoparticles is studied by means of atomistic modeling within the framework of the molecular dynamics method. The considered model consisted of two nanoparticles, each of which contained 5398 atoms. The interaction between particles was described by means of the Leonardo-Jones pair potential supplemented by the Coulomb interaction. The paper considers the effect of temperature on the process of combining nanoparticles depending on the distance between them. Attention is paid to the deformation of PbSe particles. At the initial stage of model relaxation, diffusion processes occur along the surface of nanoparticles due to the presence of polarly charged (111) planes on the crystal surface. This process is accompanied by deformation of particles along the axis of mutual arrangement of PbSe. There is a tendency to an increase in deformation with increasing temperature. The tendency of increasing deformation with increasing distance between particles is characteristic. The presence of PbSe near the second particle leads to an increase in deformation with increasing temperature. The maximum deformation of the particles increased by 5%, compared to a single particle, where the deformation is due only to its own dipole moment.

1. Introduction

The development of the nanosystem industry stimulates the study of various materials and their properties in the transition to the corresponding nanostructured state of matter. One of these materials is lead selenide, it is actively used in thermoelectric devices, as bleachable media for solid-state lasers, narrow-gap nanoparticles based on lead selenide have expanded the photosensitivity region of the polymer matrix to the near-IR range, etc. [1-5]

The unique effect of multiple generation of excitons, a controlled change in the band gap with varying sizes of nanostructures, an extremely high dielectric constant and high mobility of charge carriers significantly expand the prospects for the use of PbSe in various fields of technology, medicine, and biology [6-11].

Given the large availability of experimental and theoretical data [12-15] on the behavior of individual PbSe nanoparticles, the mechanisms of structural rearrangements and the dynamics of individual lead



selenide nanoparticles remain poorly understood. This knowledge is critical not only for designing nanocrystals and nanocrystalline architectures with desired properties for various purposes, but also for controlling physical and chemical processes over a wide range at the atomic or nanometer scale. Lead selenide particles show a good tendency to combine individual crystals into more complex structures: nanorods, nano-needles, nanorings, and others. The process of combining crystals depends on many factors, among which one can distinguish: the shape and orientation in space, temperature, the environment in which the crystals are located. Taking all factors into account is an extremely difficult task.

Also, in recent years, much attention has been paid to the nonlinear dynamics of the lattice of the material under consideration, due to low thermal conductivity. It is emphasized in [16] that lead selenide can have a sufficient degree of bond anharmonicity to maintain localized eigenmodes. The authors have experimentally shown through neutron scattering a high-temperature localization in PbSe, which is not limited to isolated modes. The cessation of the propagation of optical phonons coincides with the unusual sharpness of the longitudinal acoustic mode due to the loss of phase space during scattering [16]. In [17], the authors paid attention to the same issue from the standpoint of ab initio calculations, which explicitly take into account strong anharmonicity, and a computationally efficient stochastic sampling scheme in the phase space. Strong anharmonicity manifested itself in the observation of an internal localized mode, which is formed at acoustic frequencies.

The appearance of works focused on the practical application of PbSe in various devices indicates its importance for a number of fields of science and technology. Recent works [18] talk about the prospects of using lead selenide in devices for generating energy at room temperatures. The authors of [19] propose the manufacture of highly sensitive IR detectors based on PbSe.

In studies of lead selenide, experimental methods are successfully used, as evidenced by the examples given above. At the same time, it is extremely difficult or impossible to use experimental methods to study the dynamics of fast processes or features at the atomic level. In this case, it seems appropriate to use the method of computer modeling. This approach has also worked well for PbSe studies. Both ab initio approaches and simpler ones based on pair interaction are used [20].

In this work, the interaction of two nanoparticles is studied by the method of atomistic modeling within the framework of the method of molecular dynamics. The effect of temperature on the process of combining nanoparticles depending on the distance between them is considered. Attention will also be paid to the lattice dynamics and manifestations of bond anharmonicities in the processes under consideration.

2. Model and experimental technique

The model consisted of two nanoparticles, the size and shape of a truncated cuboctahedron [22], proposed in [12], each of the nanoparticles contained 5398 atoms (figure 1). The interaction between particles was described using the Leonardo-Jones pair potential, supplemented by the Coulomb interaction:

$$U_{ij}(r_{ij}) = U_{Coulomb}(r_{ij}) + U_{LJ}(r_{ij}) = \frac{q_i q_j}{4 \cdot \pi \cdot \epsilon_0 \cdot r_{ij}} + 4 \cdot \epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (1)$$

The potential parameters were taken from [20]: $q_{Pb} = 1.29 \text{ e}$, $q_{Se} = -1.29 \text{ e}$, $\sigma_{Pb} = 3.29 \text{ \AA}$, $\sigma_{Se} = 4.36 \text{ \AA}$, $\epsilon_{Pb/kB} = 30.0 \text{ K}$, $\epsilon_{Se/kB} = 45.3 \text{ K}$, where kB Boltzmann constant. The Lorentz-Berthelot mixing rule was used to describe the interaction of Pb and Se with the Leonardo-Jones potential. The potential cutoff value was $12 \text{ \AA}$. The Coulomb part was calculated using the multilevel summation method [21].

Calculations based on this potential showed excellent agreement with experimental and quantum mechanical results in terms of lattice parameters and elastic constants. In addition, it was used to reveal qualitatively correct images of changes in particle shape as a result of melting at finite temperatures [12].

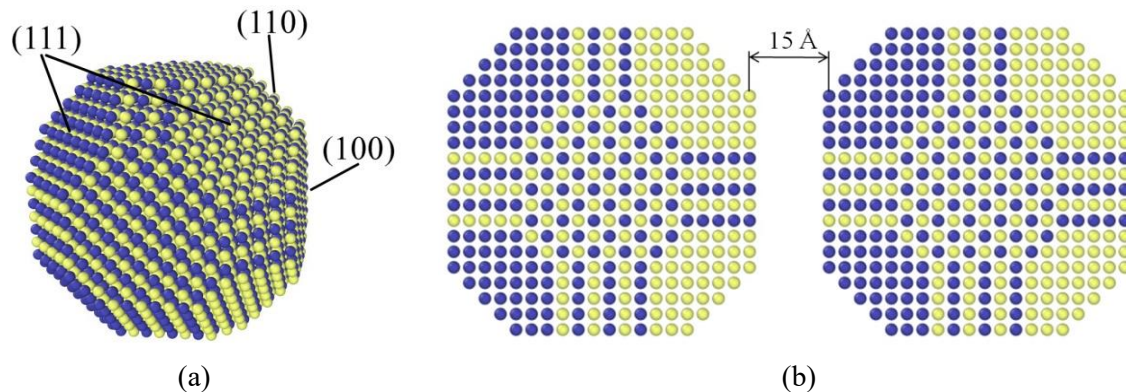


Figure 1. a) Model of PbSe nanoparticle with 26 faces, b) example of mutual arrangement of nanoparticles, plane view (001).

Nanoparticles with a strong electric dipole with a structure of the NaCl type, which PbSe possesses, are formed as a result of an uneven distribution of polar (111) planes on the crystal surface. Results were also obtained indicating the appearance of a dipole moment caused by the violation of the symmetry of the PbSe crystal [12]. This is due to the availability of experimental data and the formation of a sufficiently strong dipole moment for such a plane configuration.

The system of two nanoparticles was constructed in such a way that the interaction force caused by the electric dipoles of the particles was maximal (figure 1b). The distance between the particles was varied from 10 to 40 Å, with a step of 3 Å. The temperature range for each of the distances was chosen from 100 to 650 K, where the maximum heating temperature is slightly less than 0.5 Tm for PbSe. The temperature step for different experiments at the same distance between particles was 50 K. To maintain the specified temperature, the canonical NVT ensemble was used, i.e. a statistical ensemble corresponding to a physical system that exchanges energy with the environment (thermostat) being in thermal equilibrium with it, but does not exchange matter, since it is separated from the thermostat by a partition impermeable to particles. The Nose-Hoover thermostat was used, the effect of the thermostat on the particles of the system under study is described using non-conservative forces that depend on the momenta of virtual particles. The advantage of the Nose-Hoover thermostat is its time reversibility and correct description of the simulated ensemble. Modeling was carried out using the LAMMPS molecular dynamics package [23]. The OVITO software was used for visualization [24].

3. Results and discussion

At the initial stage of model relaxation, diffusion processes occur along the surface of nanoparticles due to the presence of polarly charged (111) planes on the crystal surface. This process is accompanied by deformation of particles along the axis of mutual arrangement of PbSe (figure 2).

The graph in figure 2 (b), there is a tendency to an increase in strain with increasing temperature. All points were fixed at the maximum relative deformation ϵ . The tendency of increasing deformation with increasing distance between particles is also characteristic. The presence of PbSe near the second particle leads to an increase in deformation with increasing temperature. The maximum deformation of the particles increased by 5%, compared to a single particle, where the deformation is due only to its own dipole moment.

The considered configuration of two particles leads to the formation of atomic chains between individual PbSe crystals. The formation of such bonds depended on the distance between particles and the temperature of the system. So for a distance less than 22.5 Å, such chains were formed over the entire temperature range considered. For distances between particles up to 27.5 Å, their formation is possible with an increase in temperature to 300 - 650 K. A further increase in the distance does not lead to their formation. However, some atoms, having separated at the initial stage of relaxation, can reach the neighboring particle.

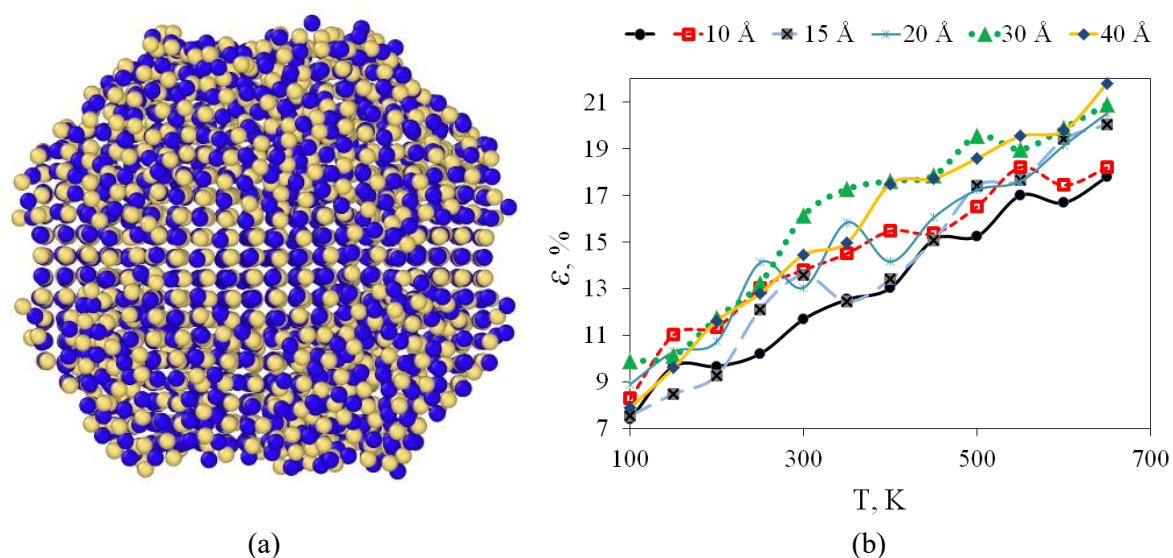


Figure 2. Nanoparticle deformation PbSe, (a) example of deformation of one of the particles at a temperature of 200 K, the initial distance between particles is 35 Å; (b) Dependence of the magnitude of the relative deformation on temperature, for a single particle (solid line with a round black marker) and for two particles located at a distance from 10 to 40 Å.

Figure 3 shows the process of combining two PbSe nanoparticles located at a distance of 18 Å. This example shows the characteristic dynamics of the process and demonstrates the formation of individual chains of atoms at all stages. It was possible to establish that, in the process of approaching the particles, the connecting chains of atoms are laid along the crystallographic directions of the $\langle 100 \rangle$ type, without the formation of defect structures in the bulk of the crystal at the junction. They increase the rate at which particles merge and decrease the likelihood of their rotation.

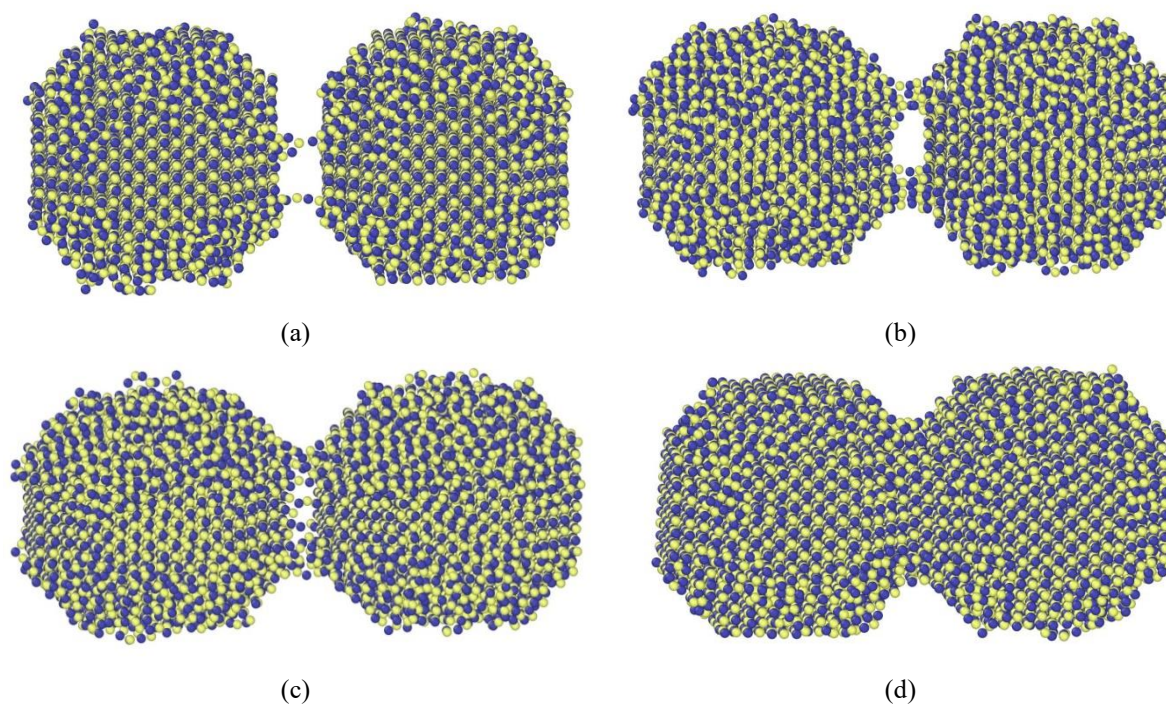


Figure 3. The process of combining PbSe particles at a temperature of 250 K, the distance between particles is 18 Å: (a) 10 ps after the start of the experiment, b) 15 ps, c) 20 ps d) 25 ps.

The temperature factor affects the process of combining particles up to 20 Å. In figure 4 (b) shows the temperature dependence of the particle merging time for different distances. The logarithmic scale is chosen for clarity only. If the distance is less than 20 Å, as the temperature rises, a decrease in the time required for the unification of particles is observed. At large distances, temperature has no obvious effect on the rate of this process. Note the peak in plot 4 (a) for a 15 Å distance between particles. This anomaly had a pronounced character for temperatures below 300 K and was stably repeated in all experiments, which was caused by a smaller deformation of the particles at these parameters.

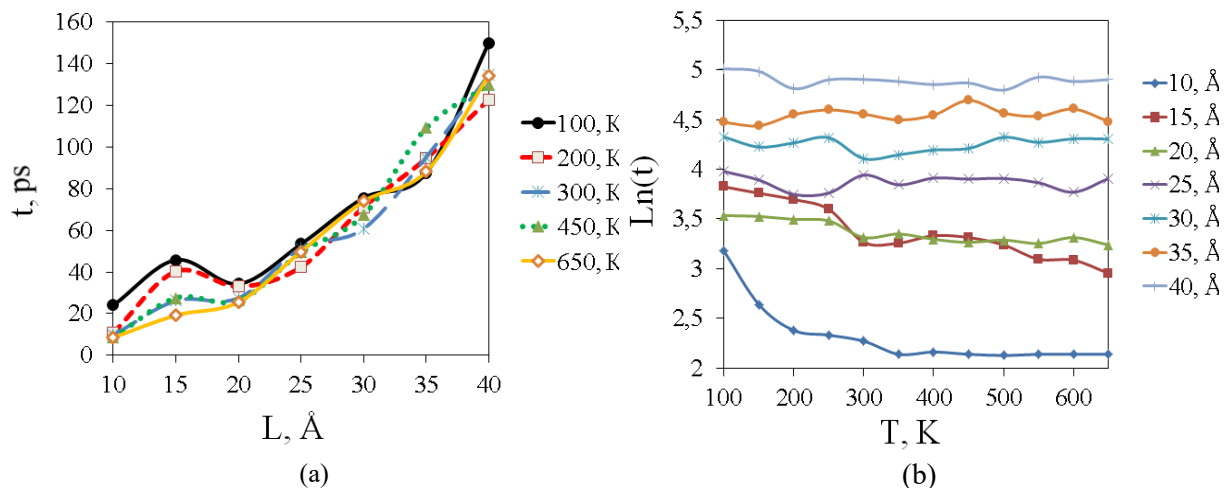


Figure 4. a) dependence of the particle merging time on the distance for different temperatures; b) tendencies of changes in the time of particle combining from temperature.

As noted in the introduction, high-temperature localized states caused by the anharmonicity of interatomic bonds were discovered in experimental studies. These states can have a significant effect on the dynamic processes in PbSe. Here, attempts were made to explicitly reveal the localization of energy on individual atoms and their groups by various methods, for example, as in works [25-27] or our last work on the study of localization and transport of energy in biatomic crystals [28]. The expediency of using the modeling method to study such processes is due to the fact that experimental work only allows one to record the presence of a peak in the crystal spectrum, and the genesis of the phenomenon is often not studied. However, it was not possible to reveal such localized states, which may be due to the features of the used interaction potential, or the specificity of localized embedded modes in the phonon spectrum of the crystal. This problem will be considered in more detail in our subsequent works.

4. Conclusion

In this work, the interaction of two lead selenide nanoparticles was studied by the method of atomistic modeling. The effect of temperature on the rate of combining of particles, as well as on the nature of their deformation, is analyzed. The dependences of the magnitude of the relative deformation of PbSe particles on temperature and the distance between them are obtained. The maximum increase in deformation at a distance of 40 Å was 5%, compared with a single particle, where the deformation is due only to its own dipole moment. The difference in the rate of the particle unification process from the experimental data is primarily due to the fact that the model particles interacted in a vacuum, and the experimental ones in a medium. The work also outlines the prospects for studying embedded localized modes and their physical nature in a PbSe crystal.

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