Abstract

Metadynamics, a powerful computational method to accelerate rare events and explore the free energy of complex polyatomic systems [1], is used to study pressure-induced structural phase transformations in CdSe bulk and nanocrystals. Metadynamics allows us to simulate such transformations close to the experimental transition pressure, thus avoiding the over-pressurisation typical of conventional molecular dynamics simulations. The fourfold- to sixfold- coordinated and reverse transitions in bulk CdSe are studied [2, 3], with the shape of the simulation cell, described by its edges, as collective variables. An interesting and controversial fivefold- coordinated metastable phase is found to lie along the wurtzite (WZ) to rock salt (RS) transition path, and the transition mechanisms are analysed in detail. The zinc blende (ZB) to RS transition is also investigated. The reverse transition from RS leads to a mixed WZ and ZB stacking, as recently observed in experiments. The method is extended to nanocrystals, where the nanocrystal shape is described by the eigenvalues of the inertia tensor. Pressure is applied to the nanocrystal either by a pressure-transmitting liquid or by using an extended Lagrangian method where the nanocrystal volume is described through its gyration radii [4]. Pressure-induced fourfold- to sixfold- coordinated transformations are studied in spherical CdSe nanocrystals, as well as in cylindrical nanorods.

References

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