Theoretical investigation and DFT modelling of novel Pd_2O polymorphs using educated guess and evolutionary algorithms

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Transition metal oxides represent a significant category of materials with wide-ranging applications in technical and chemical fields. Among these, binary oxides of palladium have recently attracted significant interest due to their exceptional catalytic properties [1], particularly in industries such as automotive, pharmaceutical, and agriculture. Despite their importance, palladium oxides remain poorly characterized, with only PdO [2] and PdO_2[3] being well-recognized. In this study, we focus on the challenging task of identifying and characterizing new phases within binary palladium oxides, specifically Pd_2O. Utilizing a strategy that combines Density Functional Theory (DFT) calculations with educated guesses and evolutionary algorithms, we aim to predict and explore the structure of Pd_2O. Palladium oxide, Pd_2O has been only identified in ultrathin palladium films and cuprite structure with space group *P*n-3m was proposed [4]. However, it was not further characterized and its properties remain unknown. Therefore, in order to gain deeper insights into the properties of Pd_2O we have calculated crystal, electronic and phonon structure of the reported cubic Pd_2O phase and evaluated its thermodynamic stability using Density Functional Theory. Additionally, in combination with evolutionary algorithms for crystal structure prediction we have proposed other potential new polymorphs of Pd_2O. Our results show that Pd_2O can form various polymorphs with more favorable formation enthalpy than previous reported cuprite structure.This study not only advances the understanding of Pd_2O but also demonstrates the effectiveness of integrating theoretical methods in the exploration of poorly characterized transition metal oxides.

Research results was obtained using the computational resources procured in the national project National competence centre for high performance computing (project code: 311070AKF2) funded by European Regional Development Fund, EU Structural Funds Informatization of society, Operational Program Integrated Infrastructure.

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