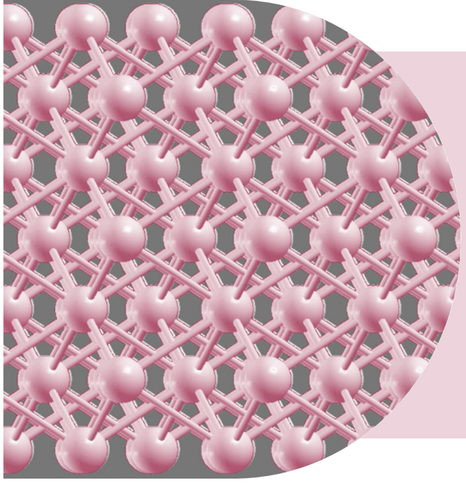

Search for atomic structures by ab initio methods and evolutionary algorithms for monatomic systems under hydrostatic pressure

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INTRODUCTION

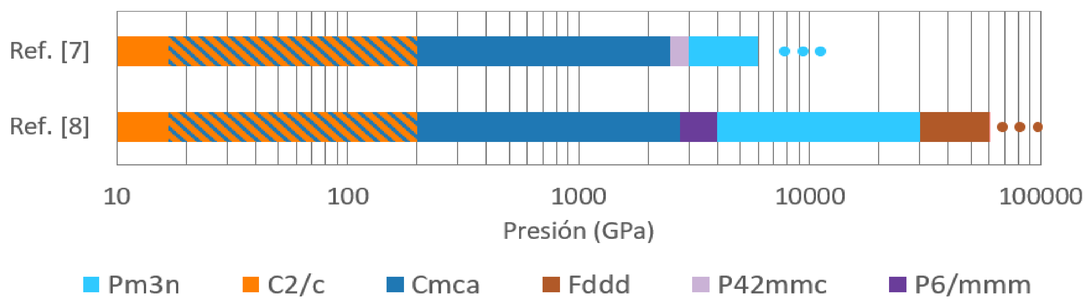
Fluorine has not been as extensively studied compared to other single-element diatomic molecules (H_2, N_2, O_2, Cl_2, Br_2, I_2). For many years, the space group of solid fluorine at ambient pressure was controversial: two different structures were proposed through spectroscopy studies and theoretical calculations [1-5]. Experiments were carried out using diamond anvil cells (DAC), but it was challenging to obtain reliable results [5]. This technical difficulty is because fluorine and the other halogen elements are volatile, corrosive, and highly reactive, which increases the complexity level when studied experimentally. Different phases have been proposed for fluorine through computational techniques [6-8]. However, the structural search components are based on previous structural information. For this reason, it is necessary to validate the phases found through the use of other unbiased structural search methods, that is, with initial structures that are not those previously reported.

METHODOLOGY

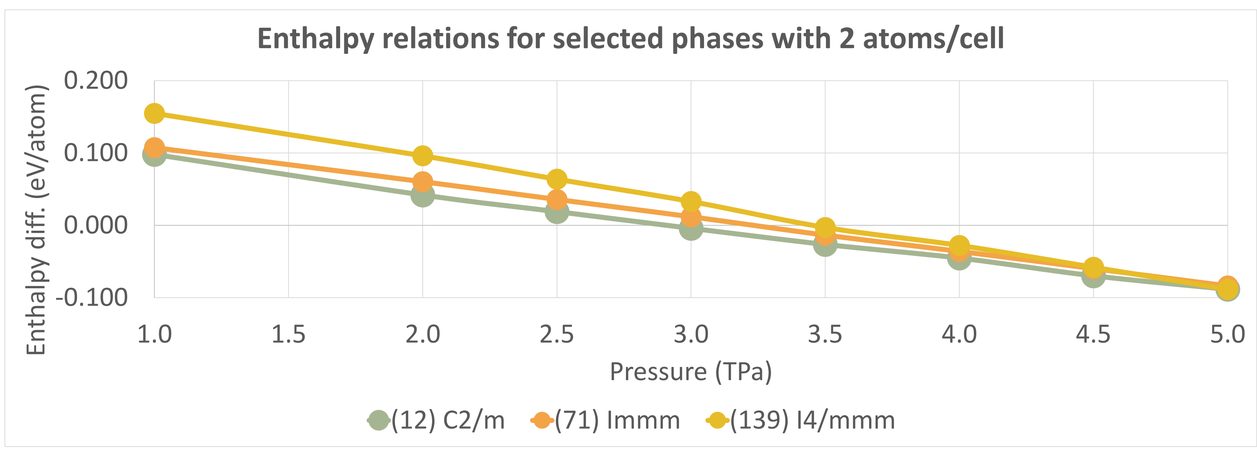
The structural searches were carried out using the USPEX package [9], and the pressure range from 1 to 5 TPa was analyzed, varying the number of atoms per cell in 2, 4, 6, 8, 12, and 16. The energies of the 28,997 structures generated were calculated using the Quantum ESPRESSO suite [10]. For the phases that were finally selected for study, we performed structural relaxation calculations to minimize the forces on the system. The Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA) functional was used, with the projector pseudopotential augmented wave (PAW) method. The cut-off kinetic energies and K-point mesh were established for each phase so that the convergence was less than 2meV per atom.

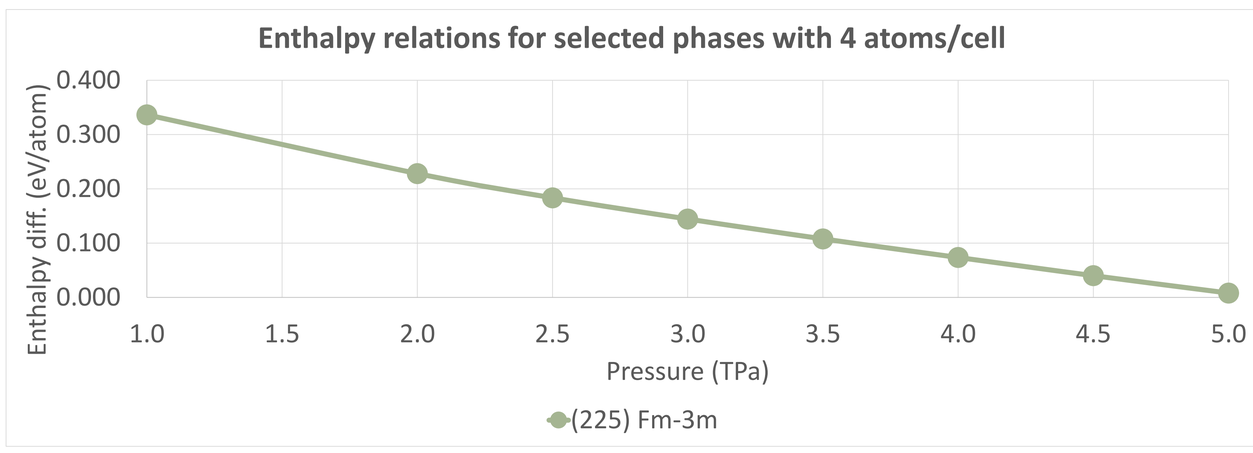
RESULTS

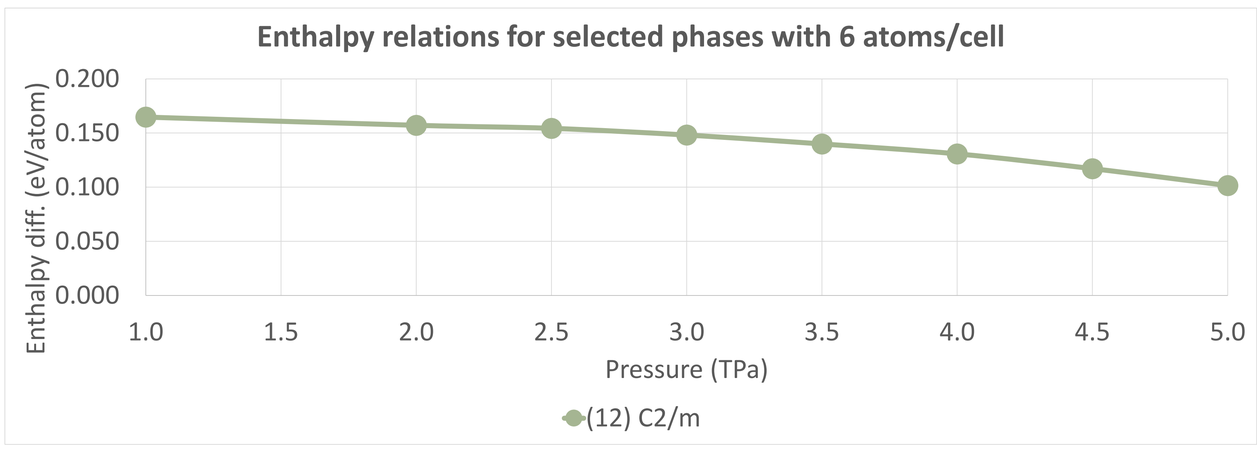
According to previous works, fluorine undergoes a *C2/c* to *Cmca* phase transformation in its molecular state: Ref. [6] indicates that the transition occurs at 8 GPa, while Ref. [7] places it at 70 GPa. This latter study suggests that the *Cmca* phase remains stable up to 2.5 TPa, while Ref. [8] set it at 2.75 TPa. The phase following the *Cmca* is different in both works: Ref. [7] maintains that it is *P42/mmc*, while Ref. [8] proposes *P6/mcc*. The subsequent phase is for both works *Pm3n*, although for Ref. [7], it occurs at 3 TPa, while for Ref. [8], it appears at 4 TPa. Finally, [8] reports an additional phase transition into *Fddd* at 30 TPa.

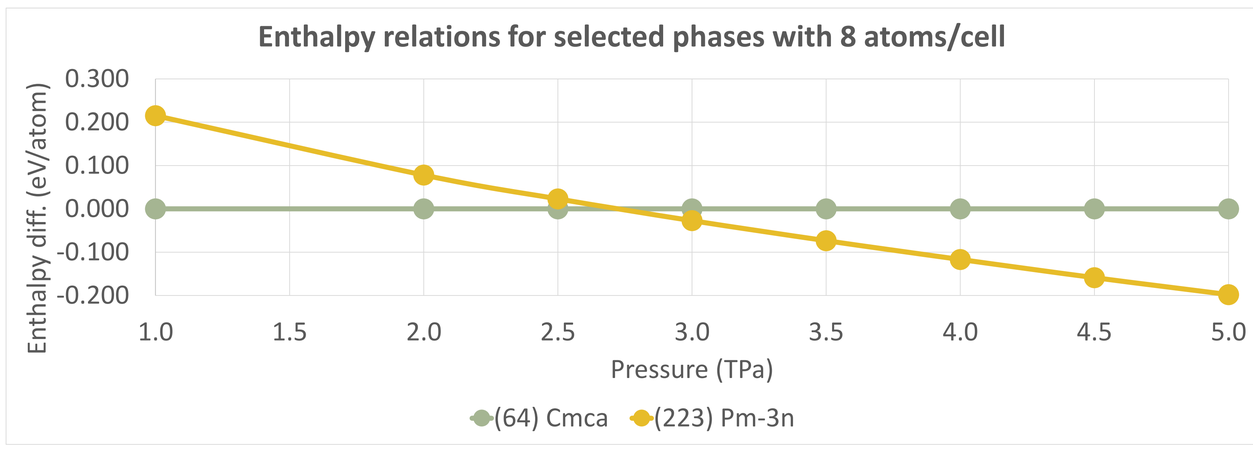


Our structural search results show new phases with lower enthalpies than those that have been reported in the recent literature for the pressure ranges of interest: C2/m-2, Immm-2, I4/mmm-2, and Pm-3n-8. Likewise, it shows the non-triviality of a simple system, which must be analyzed carefully to better understand its behavior under extreme conditions.









CONCLUSIONS AND FUTURE WORK

The enthalpy relationships that make up the preliminary results show that the structural search using evolutionary algorithms provided more stable structures than those currently reported in the literature. However, given that the post-Cmca phases were reported in the terapascal regimen, it is necessary to include thermal effects to provide the enthalpy relationships and a P-T phase diagram that provides a more realistic view of the behavior of fluorine under different conditions of pressure and temperature parameters.

AKNOWLEDGEMENTS

B. H. C-O thanks MinCiencias for its support through the Call 891 of 2020. B. H. C-O and J. A. M. thank the Vice-Rectoría de Investigaciones and the ROSMME Computer Center of the University of Cartagena for their support through internal calls.

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