# Prediction of new polymorphs of old materials from a bottom-up approach using density functional theory calculations

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Whereas high-density metastable materials polymorphs may be experimentally probed by directly altering the bulk phase (e.g via high pressure cells) the space of low-density phases is not so readily accessible. Nucleation of suitable nanoscale units provides an alternative for the production of low-density polymorphs, exemplified by the synthesis of nanoporous silicates (e.g. zeolites) where the aggregation of cluster precursors can be conveniently influenced in solution. This technique, however, is not easily transferable to all materials and we propose that, otherwise unobtainable low-density zeolite-like phases of typically dense materials may be accessible via the coalescence of "magic" cluster building blocks i.e. clusters exhibiting particularly high gas phase stability. Specifically, for two important metal oxides MO (M=Zn, Mg) and for the whole series of MX (M=Li, Na, K, Rb,Cs; X= F, Cl, Br, I) alkali halides we show, via accurate electronic structure calculations, that these materials may be stabilized as ultra-low-density zeolitic-like polymorphs constituted from magic cage-like $(MO)_{12}$ or $(MX)_{12}$ clusters with energetic stabilities rivaling —and sometimes clearly below — that of known polymorphs.[1,2] In particular, we find that the sodalite structure of LiF was not predicted in earlier studies using global optimization techniques. Interestingly enough, the energy of the LiF sodalite structure is close to one of the known form of LiF (LiF-1) which, among the polymorphs known prior to the present work, is the one with lowest density

To summarize, merging state of the art density functional calculations and a bottom-up strategy provides a complementary way to explore the energy landscape of interesting materials and allows one to predict the existence of new forms although their synthesis may represent a real challenge

1) J. Carrasco, F. Illas and S.T. Bromley, Phys. Rev. Lett., 99 (2007) 235502
2) W. Sangthong, J, Limtrakul, S.T. Bromley, and F. Illas, to be submitted