

Structure and properties of titanosilicate systems

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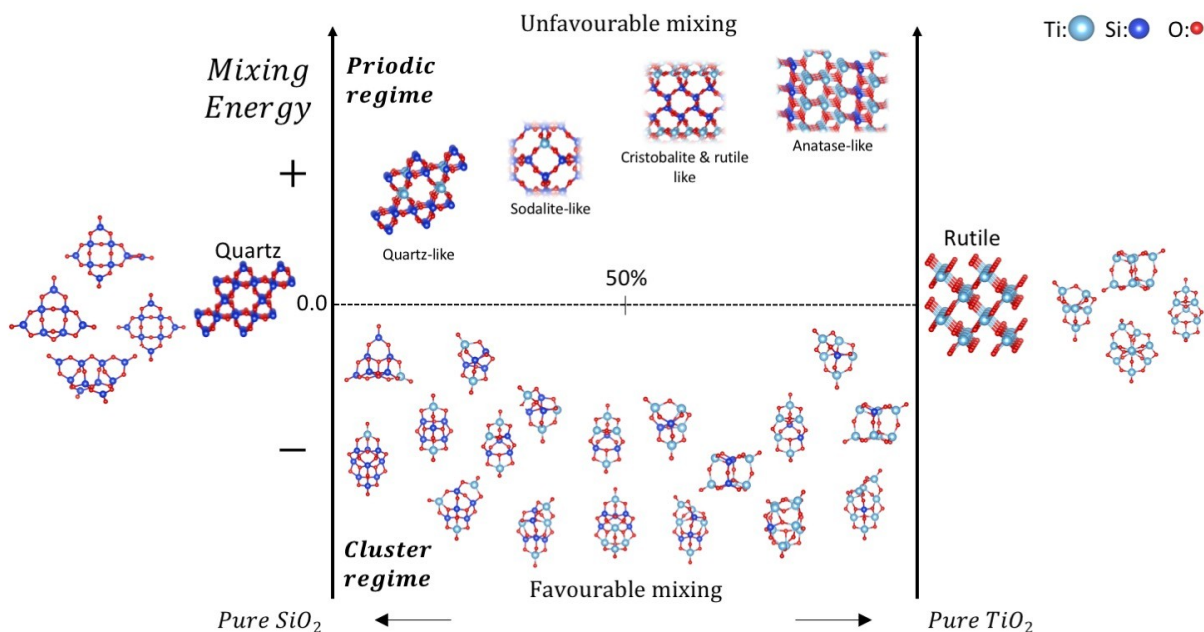
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Materials based on mixing titania (TiO_2) and silica (SiO_2), titanosilicates, represent an important class of materials widely studied and used for many applications such as an industrial redox catalyst, solar cells, self cleaning systems, selective molecular sieves, materials for removing water pollutants and photocatalysts for many reactions [1-3]. In many applications titanosilicates not only take advantage of the properties of pure titania (semiconductor and catalytic support) and silica (high thermal stability and high mechanical strength) but from the symbiotic properties which emerge from the TiO_2 - SiO_2 interaction of (e.g. formation of new catalytic sites). It is relatively difficult to synthesize homogeneous TiO_2 - SiO_2 mixed oxides material due to their tendency to aggregate and separate into two phases. So far, the homogeneous mixing seems to be only possible in crystalline systems, by the inclusion a very small percentage of TiO_2 in a silica framework, and in glassy materials with higher TiO_2 : SiO_2 ratios. Such bulk phase titanosilicates are metastable (energetically unstable but kinetically stable) with respect to the separate pure polymorphs (quartz and rutile). At the nanoscale, however, the mixing of these two materials is energetically favorable and our aim is to understand why this happens and at which size it starts to become metastable.



We first selected a bunch of titanosilicate polymorphs and then we calculated their relative stability by Density Functional Methods (DFT) with respect to the pure silica and titania crystalline systems (respectively α -quartz and rutile). At later time, we considered titanosilicates at nanoscale selecting different cluster sizes (up to 24 MO_2 units where $\text{M}=\text{Ti},\text{Si}$) and TiO_2 ratio. The Monte Carlo Basin-hopping global optimization algorithm [4] was used in order to find reasonable low energy structures for cluster scale systems. A selection of low energy isomers is subsequently refined at a DFT level of theory. Our results point to a number of important factors which determine how favourable the $(\text{TiO}_2)_N\text{-(SiO}_2)_M$ mixing is and at which size it becomes unfavourable. We hope to use these atomic scale insights to design new cluster-assembled titanosilicate materials, which, depending on the clusters employed, could be optimized for a range of applications.

References

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