Zeolites are framework materials with porosity at the molecular scale formed by the complete corner sharing of tetrahedral aluminosilicate groups. The aluminosilicate framework is negatively charged and there are charge-balancing cations inside the pores bonded to the oxygen atoms of the tetrahedra. Like many framework materials, the structures are very flexible and are known to undergo pressure-induced amorphisation at relatively low (<10 GPa) pressures. The amorphisation should not involve significant (Si,Al)–O bond breaking at these pressures but loss of long-range order due to severe and non-correlated distortions of the (Si,Al)–O–(Si,Al) bonds to form network glasses. We [1] and others [2,3] have recently started to use Pair Distribution Function analysis of total scattering data to study the quenched glasses. The goals of our work are both to understand the mechanism of amorphisation and nature of the glass, in particular to determine to what extent it might still have some of the secondary structural building units and porosity of the crystalline precursor.

All work published to date is based on ex situ studies of quenched glasses. We have now collected in situ high pressure total scattering data on several samples of zeolite A with different charge balancing cations as well as the pure silica polymorph ITQ-29. The analysis from this series allows us to determine the effects that the cations inside the pores have on the amorphisation mechanism and also, by comparing the glasses at pressure and then quenched back to room pressure, to study the reversibility of the process.

Accurate thermodynamics in the quasiharmonic approximation

Alberto Otero-de-la-Rozana, Victor Luaha Departamento de Química Física y Analítica, Universidad de Oviedo, c/Julián Clavería 8, 33006 Oviedo, (Spain). E-mail: alberto@carbano.quimica.uniovi.es

Is it possible to calculate the thermodynamic properties of a solid with accuracy that rivals that of the experimental measurements for a wide range of pressures and temperatures? We discuss in this report the three main elements that can drive systematically to that result: (i) The density functional perturbation theory (DFPT) by Baroni et al [1] and its implementation in codes like Quantum Espresso [2] has made possible the ab initio calculation of thermodynamic properties of solids under the quasi harmonic approximation (QHA); (ii) The average of strain polynomials [3] is used to fit faithful and systematically the energy versus volume data, providing the best derivatives available and a statistically relevant estimation of the errors; (iii) The systematic error of the calculations due to the approximate nature of the exchange and correlation functional is repaired through an empirical energy correction scheme (EEC) based only in two experimental data (the equilibrium volume and bulk modulus). Several examples of the extraordinary success of this recipe are discussed.