Stability and phase transitions under high pressure in silicon clathrates

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Silicon clathrates are nanostructured cage-like materials that allow for high intercalation. As a consequence, their physical properties are depending on the nature of the guest atom trapped in the Si_{20}, Si_{24} and Si_{28} cages constituting their covalent sp^3 network. In this work, the high-pressure properties of different type of silicon clathrates (type-I M_xSi_{46}, type-II M_xSi_{136}…) have been studied by X-ray diffraction (ESRF, ID30 and ID09) and X-ray absorption spectroscopy (ESRF, ID24 and BM29). The case of type-I Ba_8Si_{46} [1] and the effect of the substitution of the guest - or host - atoms were particularly investigated [2].

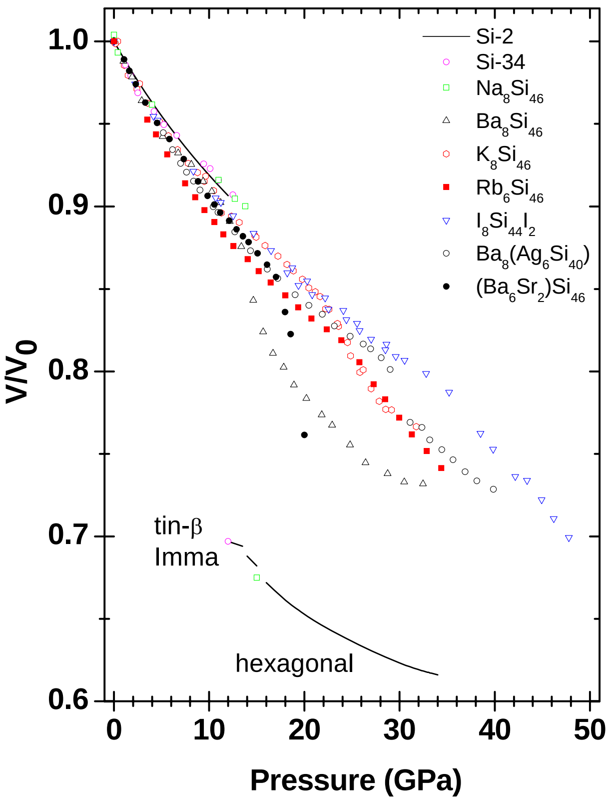

Figure 1: Relative volume as a function of pressure in type-I and type-II silicon clathrates.

First of all, it is shown that the clathrate structure has a pressure stability domain up to 4 times bigger than the Si-diamond one.

Secondly, we observed that clathrates intercalated with light atoms (Na) or empty clathrates give rise to a 1st order phase transition. For large atoms (K, Rb, Cs, Sr, Ba) in the cages, an original phase transition is found, i.e. a 2nd order transition based on an isostructural volume collapse. Rietveld analysis of the Ba8Si46 XRD data shows the homothety of the contraction of the host lattice after the structural transition (~ 11.5-14 GPa).

EXAFS at the Ba K-edge demonstrates that the Ba atom is at the center of cages, with a precision of 0.3 Å, at least up to the volume collapse pressure. Finally, the position of the Ba L3-edge shows a jump at about 5 GPa demonstrating a change of hybridization of the Ba-5d electrons. This change is associated to the disappearance of low energy Raman modes [3].

References
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