

# High pressure synthesis of novel, zeolite based nano-composite materials

M Santoro<sup>1,2</sup>, F A Gorelli<sup>1,2</sup>, R Bini<sup>2,3</sup>, J Haines<sup>4</sup>, O Cambon<sup>4</sup>, C Levelut<sup>5</sup>, A van der Lee<sup>6</sup> and G Garbarino<sup>8</sup>

<sup>1</sup> CNR-INO, 50019 Sesto Fiorentino, Italy

<sup>2</sup> LENS, 50019 Sesto Fiorentino, Italy

<sup>3</sup> Università di Firenze, Dipartimento di Chimica, I-50019 Sesto Fiorentino, Italy

<sup>4</sup> ICGM, Equipe C2M, UMR 5253, CNRS, UM2, 34095 Montpellier, France

<sup>5</sup> LCC, UMR 5221, CNRS, UM2, 34095 Montpellier, France

<sup>6</sup> IEMM, UMR 5635, CNRS, UM2, 34095 Montpellier, France

<sup>7</sup> ESRF, 38343 Grenoble, France;

Email: santoro@lens.unifi.it; mario.santoro@ino.it

**Abstract.** Zeolites exhibit an immense range of applications, such as those in the chemical industry, electronics and photonics among others. We used non-catalytic zeolites in an entirely new fashion. In fact, high pressure (0.5-26 GPa) chemical reactions of simple molecules in the pores of a pure SiO<sub>2</sub> zeolite, silicalite were performed in the diamond anvil cell to obtain unique nano-composites with drastically modified properties. These materials were investigated using a combination of X-ray diffraction and optical spectroscopy. We will first show how silicalite can be easily filled by simple molecules at high pressures and how this filling deactivates pressure induced amorphization of the silica framework. We will then present a silicon carbonate phase synthesized by reacting silicalite and molecular CO<sub>2</sub> that fills the nano-pores, at 18-26 GPa and 600-980 K; the resulting compound is slightly metastable at room pressure. On the other hand, a nano-composite, which is stable at room temperature and pressure, is obtained by photopolymerizing ethylene at 0.5-1.5 GPa under UV (351-364 nm) irradiation in the channels of silicalite. The structure of this material is characterized by single polyethylene chains adapting very well to the confining channels, which significantly modifies the physical properties of the silicalite framework. These findings may pave the way to the high pressure synthesis of a unique generation of technological materials.

## 1. Introduction

Meso/micro-porous solids such as zeolites are complex materials exhibiting an impressive range of applications, including molecular sieve, gas storage, catalysis, electronics and photonics [1-11]. We used these materials, particularly non-catalytic zeolites in an entirely different way. In fact, we performed high pressure (0.5-26 GPa) chemical reactions of simple molecules on a sub-nanometer scale in the channels of a pure SiO<sub>2</sub>, zeolite, silicalite to obtain unique nano-composite materials with drastically modified physical and chemical properties. This material was investigated using a combination of X-ray diffraction (XRD), and Raman and IR spectroscopy in the diamond anvil cell (DAC).

Zeolites are micro-porous, crystalline, inorganic solids made of corner-sharing SiO<sub>4</sub> and AlO<sub>4</sub> tetrahedra with strong acid character and catalytic properties. At one end of this class, there is silicalite,



which is an electrically neutral, non-catalytic zeolite. This material is characterized by a framework of four-, five-, six- and ten- membered rings of corner-sharing  $\text{SiO}_4$  tetrahedra forming interconnected, mutually orthogonal straight and sinusoidal 5.5 Å diameter channels (see [12] and references therein), as shown in the inset of figure 1.

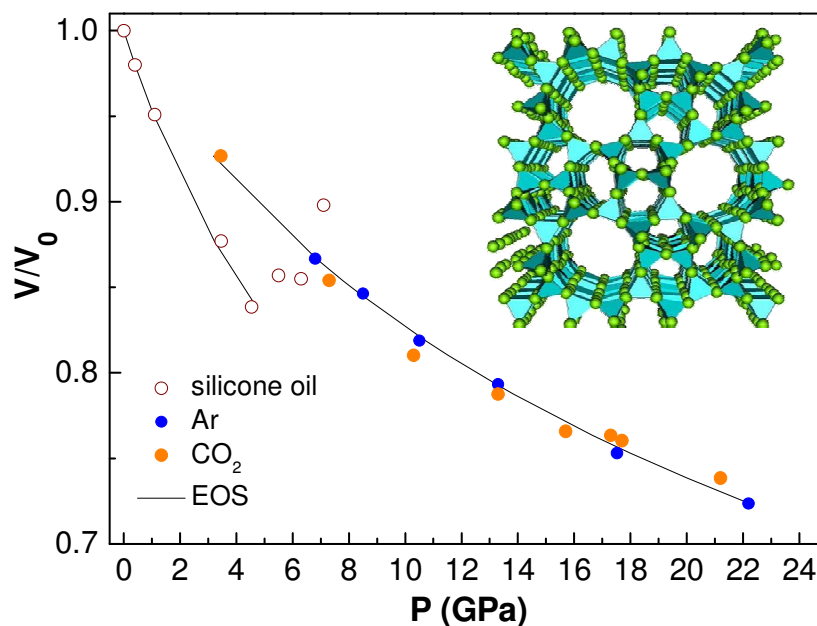
Here, we will first briefly show how silicalite can be easily filled by simple molecules such as Ar,  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$ , among others, from the fluid phases at high pressures, and how this efficient filling deactivates the well known pressure induced amorphization of the silica framework up to at least 25 GPa [13]. These results characterize the overall structural stability of our ideal, chemical nano-laboratory: the silicalite nano-channel. We will then present the reaction of nano-confined  $\text{CO}_2$  with silicate. This idea was inspired by the now well established discovery over the past 15 years, that pure  $\text{CO}_2$  undergoes several transformations above 30 GPa from the molecular solid phases to non-molecular, covalent extended materials, both crystalline and amorphous, similar to the  $\text{SiO}_2$  polymorphs in some respects. As a matter of facts, the crystalline, non molecular  $\text{CO}_2$  phases contain carbon in four-fold coordination by oxygen [14-17], whereas a mixture of  $\text{CO}_4$  and  $\text{CO}_3$  units have been found in a glassy form that has been named carbonia [18-20]. Here we will show that a crystalline, silicon carbonate phase can be synthesized by reacting silicalite and molecular  $\text{CO}_2$  that fills the nano-pores, at 18-26 GPa and 600-980 K; after the synthesis the compound is temperature quenched and it was found to be slightly metastable at room conditions [21]. On the other hand, a spectacular crystalline nano-composite, which is stable under ambient conditions, is obtained by photo-polymerizing ethylene at 0.5-1.5 GPa under UV (351-364 nm) irradiation in the channels of silicalite [22]. This investigation was also stimulated by the discovery that pure simple hydrocarbons, such as acetylene [23] and ethylene [24, 25] among others, can be polymerized by the application of high pressures, sometimes in combination with UV light irradiation, without the use of catalysts and radical initiators. The structure of our polyethylene/silicalite composite contains single polyethylene chains adapting very well to the confining channels, which results in at least two kind of significant changes with respect to the original silicalite host: (i) increases in bulk modulus and density, and (ii) changes in the thermal expansion coefficient from negative to positive. Mechanical properties may thus be tuned by varying the amount of polymerized ethylene.

Our findings may allow the high pressure, catalyst free synthesis of a unique generation of technological, functional materials based on simple hydrocarbons polymerized in confining meso/micro-porous solids.

## 2. Structural stability of silicalite under pressure

We have recently shown that the insertion of simple molecules such as Ar,  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  in the channels of silicalite deactivates pressure induced amorphization (PIA) in this zeolite, up to at least 25 GPa [13, 22]. The molecular systems were loaded in DACs cryogenically in the liquid phase at 1-30 bar, together with silicalite. Raman and IR spectroscopy in DACs were used for identifying nano-confined  $\text{CO}_2$  [21] and  $\text{C}_2\text{H}_4$  [22]. As a matter of facts, the vibrational peaks of the confined substance are shifted by 10-50  $\text{cm}^{-1}$  and also exhibit a larger line width with respect to those of the bulk substance, which is due to the interaction with the silicalite nano-walls.

Raman spectroscopy and synchrotron powder XRD (ESRF-ID27,  $\lambda=0.3738$  Å) have been used as probes of the PIA [13]. The compression of silicalite-1-OH, which contains traces of hydroxyl groups, and of hydrogen-free silicalite-1-F obtained from SOMEZ (France) was investigated with non-penetrating (silicon oil) and penetrating (Ar or  $\text{CO}_2$ ) pressure transmitting media (PTM). The XRD analysis shows that in silicalite-1-OH using silicone oil, a monoclinic-to-orthorhombic phase transition occurs at close to 1 GPa with very small volume change. Progressive PIA is then observed, which is complete just above 8 GPa. Structural data were used to obtain an equation of state (figure 1) with a bulk modulus  $B_0$  of 18.8(5) GPa, which is higher than in silicalite-1-F:  $B_0=13.6$  GPa. The difference between the compressibility of the two materials and the points between 5.5 and 7.1 GPa may be due to nonequilibrium effects, as the material was in the process of undergoing amorphization, which can give rise to local depressurization [12].



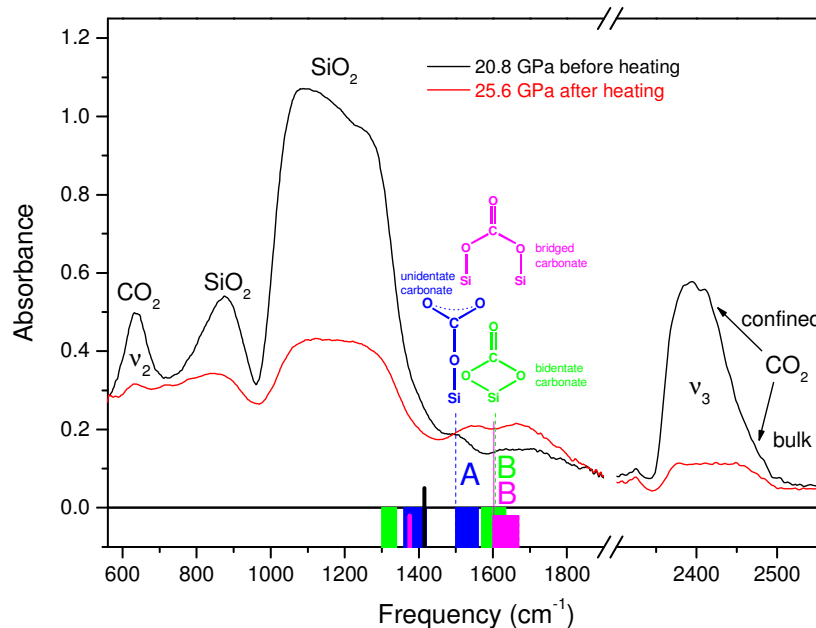
**Figure 1.** Relative volume of silicalite-1-OH as a function of pressure, using silicon oil, Ar or CO<sub>2</sub> as PTM; solid lines are fits to the Birch-Murnaghan equation of state. Inset: crystal structure of silicalite.

Very different behavior is observed in the presence of CO<sub>2</sub> or Ar as the PTM (figure 1). The relative intensities of the Bragg peaks of silicalite are very different as a result of changes in structure factor in the presence of the guest molecules. The structure is orthorhombic at the first high-pressure points after loading of the DAC. Silicalite-1-OH was found to be significantly less compressible in CO<sub>2</sub> or argon, because of the penetration of these species into the pores of the structure. The compressibility and the overall equations of state in the two cases are very similar, indicating that pore filling is comparable for the two species. The common bulk modulus is:  $B_0=35.9(4)$  GPa, which is almost identical to that of  $\alpha$ -quartz [26] indicating direct compression of the framework. In contrast to the experiment in silicone oil, here there is no evidence of PIA in filled silicalite up to at least 22 GPa (25 GPa with Raman spectroscopy). In addition, there is no increase in the width of the diffraction peaks up to these pressure. The changes in structure factors, the increase in bulk modulus, the isotropic compression, and the absence of PIA are consistent with complete filling of the pores by the PTM (i.e., CO<sub>2</sub> or Ar), which is in equilibrium with the PTM outside the pores. Computer simulations provide further insight into the mechanisms of filling the nano-channels with simple molecules and removing the PIA [27, 28].

### 3. A silicon carbonate phase obtained by reacting silicalite and nano-confined CO<sub>2</sub>

Very thin, about 1  $\mu\text{m}$ , sample mixtures of silicalite and CO<sub>2</sub> were compressed to about 20 GPa and then heated to 700-750 K to induce the chemical reaction between confined CO<sub>2</sub> and SiO<sub>2</sub> [21]. In the IR spectrum of the temperature quenched material (figure 2) the peaks of silicalite are reduced by about 50% of the original intensity, and the peaks of confined CO<sub>2</sub> almost completely vanished. In parallel, two new strong peaks A and B appeared. Therefore, it is clearly shown that indeed silicalite and confined CO<sub>2</sub> react with each other and a new product substance is formed, identified by peaks A and B. The overall transformation is reversible upon lowering the pressure, and remnants of the new material disappear in a few days at room pressure. The assignment of peaks A and B to C-O stretching modes of silicon carbonates is very straightforward ([21] and references therein). In fact, it is well known that CO<sub>2</sub> forms carbonates by absorption at ambient pressure on the surface of basic metal oxides and a variety of zeolites that contain transition, alkali or alkaline earth metals. Carbonates are also formed in CO<sub>2</sub>-bearing, high silica, aluminosilicate glasses, where the cation is tetrahedrally coordinated by

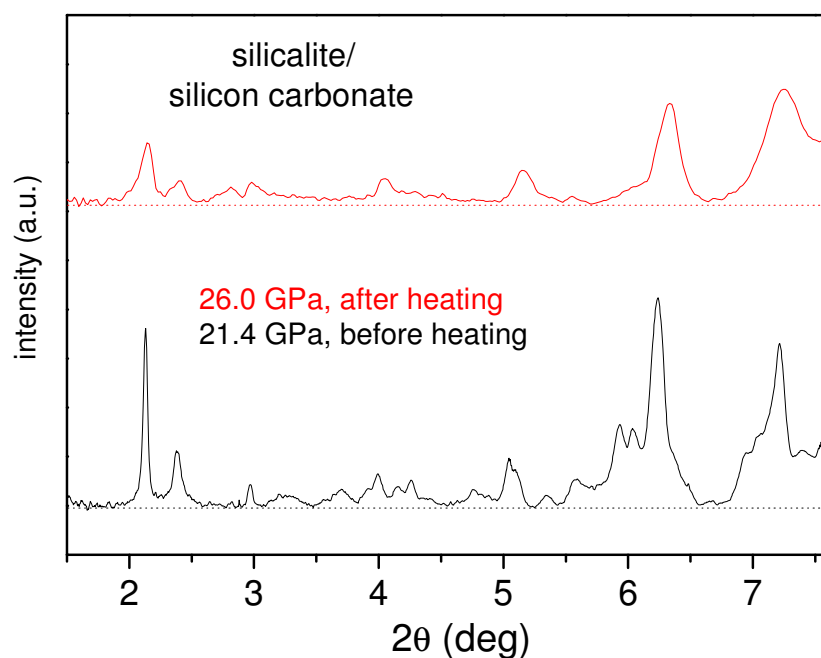
oxygen. These carbonates exhibit unidentate, bidentate or bridged structures (figure 2), where the doubly degenerate IR stretching mode of the free  $\text{CO}_3$  ion splits in two bands either side of the unperturbed frequency ( $1415\text{ cm}^{-1}$ ). Remarkably, the high frequency components of these carbonate structures fit fairly well to the ambient pressure extrapolated frequencies of peaks A and B, thereby showing that the reaction of confined  $\text{CO}_2$  with silicalite results indeed in the formation of unidentate, bidentate and bridged carbonates, involving either one or two framework silicon atoms.



**Figure 2.** High pressure IR spectra before and after the heating to 740 K of a mixture of silicalite and  $\text{CO}_2$ , showing the formation of silicon carbonate. The A and B peaks are assigned to unidentate (A), bidentate (B) and bridged (B) silicon carbonate species. Vertical black stick: frequency of the IR stretching mode of the free  $\text{CO}_3$  ion. Bars: spectral ranges, at ambient pressure, of the split high and low frequency components of the IR stretching mode of the free  $\text{CO}_3$  ion, as found in unidentate (blue), bidentate (green) and bridged (pink) carbonates, obtained from  $\text{CO}_2$  adsorption on metal oxides and dissolution in silicate melts. Vertical lines: room pressure extrapolated frequencies of the A and B peaks.

As an additional test of the chemical reaction and of the nature of the compound, we measured the XRD patterns (figure 3) on a mixed  $\text{CO}_2$ /silicalite sample compressed to 21.4 GPa and then heated to 723 K [21]. The Bragg peaks of orthorhombic silicalite progressively broaden upon increasing temperature. This is a clear indication of the chemical reaction between confined  $\text{CO}_2$  and silicalite, as diffraction peaks should instead sharpen because of the usual temperature enhancement of the crystal quality and relaxation of any deviatoric stress present. Loss of  $\text{CO}_2$  followed by PIA upon increasing temperature is ruled out because the structure of silicalite does not change, and because the broadening of Bragg peaks was reversible upon subsequent pressure release, while PIA is irreversible. The reversible broadening of Bragg peaks shows the overall reversibility of the reaction, in very good agreement with IR results. The results show that the chemical reaction yields a product that is a highly strained crystal, which still exhibits the silicalite structure. This is what one should expect, since the carbonates form at the pore surface, which in turn should not alter the pore arrangement within the unit cell, but affect the long range periodicity of the structure. In fact, the solid is strained and the coherence length is reduced to 8-10 nm, at the maximum temperature, as deduced from the peak width. This is evidence that the

carbonate groups form in a random manner without any long range order. They can also be expected to induce local geometrical distortions to the framework. Surprisingly, no peaks of stishovite, the six-fold coordinated crystalline silica are observed. Stishovite is the thermodynamic stable phase of silica above 9 GPa, and it easily forms upon heating cristobalite to 570 K, at similar pressures. The fact that we are left with silicon carbonate, instead of stishovite and molecular CO<sub>2</sub>, is evidence of the high chemical stability of this compound.



**Figure 3.** High pressure, synchrotron (ESRF-ID27,  $\lambda=0.3738$  Å) XRD patterns of a silicalite/CO<sub>2</sub> mixture before and after the heating to 723 K, showing the formation of a highly strained, disordered crystal. Sample thickness: about 20  $\mu\text{m}$ . At angles higher than 7.5° the diffraction pattern is dominated by the peaks of bulk, molecular CO<sub>2</sub>.

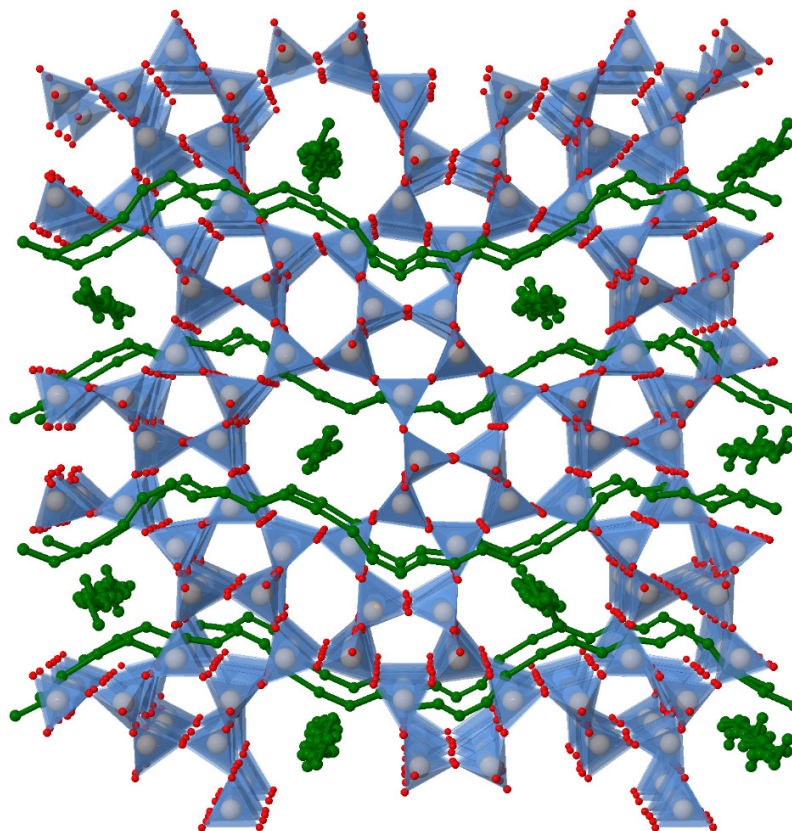
#### 4. PESIL: a nano-composite obtained by polymerizing ethylene in the channels of silicalite

A very intriguing aspect of porous solids is the ability to drive the formation of confined polymers with remarkable physical properties (see references 12-20 in [22]). Polymerization is usually performed by using catalysts and radical initiators, which are either supplied by the pore walls or are added to the pores together with the reactants. We performed confined polymerization of ethylene in silicalite, using only high pressures and UV light irradiation [22]. We then succeeded to push the effect of confinement on polymerizing matter down to the sub-nanometer scale, while avoiding any catalytic effects from the pores, which in turn led us to better understand the effect of confinement *per se*. Unique nano-composite materials could be synthesized by using these “green chemistry” synthesis routes. Here we refer to our nano-composite as PESIL, from PE (polyethylene) and SIL (silicalite).

We compressed supercritical fluid ethylene to 0.5-1.5 GPa, at room temperature, together with either polycrystalline or single crystal silicalite-1F. Based on Raman and XRD measurements it was found that ethylene completely filled the pores of silicalite, as was also observed previously using Ar and CO<sub>2</sub>. The polymerization of ethylene was then performed at 0.5-1.5 GPa under UV irradiation (351-364 nm) for a few hours with a power density of 1.6-3.2 W/mm<sup>2</sup>. The obtained PESIL was recovered at ambient pressure. Polymerization and PESIL were investigated by optical spectroscopy and XRD. Particularly, IR spectroscopy allowed us to easily identify confined polyethylene in the channels of host silicalite, the absorption peaks of which are shifted by 5-30 cm<sup>-1</sup> with respect to those of bulk polyethylene. Also,



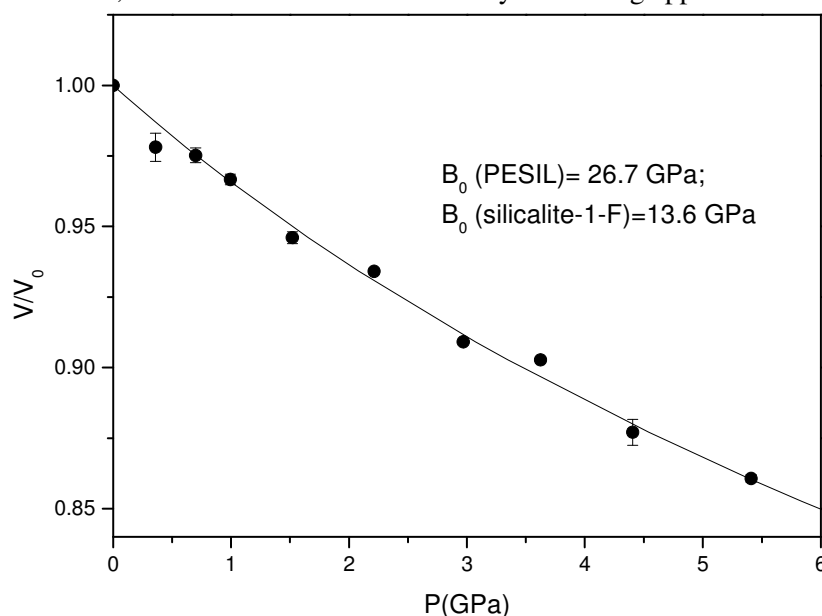
IR peaks of the confined polymer are much broader, which is a first hint that some strain is imposed on the polymeric chains due to the high degree of confinement.



**Figure 4.** Structure of PESIL  $((\text{SiO}_2)_{96}(\text{C}_2\text{H}_4)_{34})$ , space group  $Pnma$ , view along **b**) obtained by single crystal XRD (Cu  $K\alpha$  radiation,  $\lambda=1.54185$  Å). Blue polyhedra:  $\text{SiO}_4$  tetrahedra; chains of green spheres (C atoms): single polyethylene chains. Hydrogen atoms are not shown.

The crystal structure of PESIL was determined using single crystal XRD data obtained from a typical sample recovered at ambient pressure [22]. Starting from the  $Pnma$  structural model for the  $\text{SiO}_2$  framework, the C atoms were located from Fourier difference maps giving a total of 68 C atoms per unit cell. The resulting structure is unique (figure 4) in terms of the arrangement of single polyethylene chains within the confining channels. Four single, ideally infinite polyethylene chains form inside the unit cell of silicalite, each having 17 C atoms per unit cell, and adapt fairly well to the shape of the ten-membered ring channels. However, nano-confinement imposes a high degree of strain on these chains. As a matter of facts, two straight, zig-zag chains lie in the straight channels along **b** with the carbon atoms remarkably displaced from the plane containing what should be the ideal zig-zag skeletal C chain [29]. The other two chains lie in the two sinusoidal channels in the  $ac$  plane. In this case, not only do the carbon atoms deviate from the skeletal plane, but the chains are also sinusoidal in order to follow the sinusoidal shape of the confining channels. Confined polyethylene is not commensurate with the host channels, because of the strong strain related disorder. Another spectacular aspect of PESIL is the change found in the structure of the silicalite framework with respect to that of pure, ambient pressure monoclinic silicalite. As in the case of silicalite filled by Ar and  $\text{CO}_2$  at high pressures, the unit cell metric is now almost pseudo-tetragonal with the  $a$  and  $b$  lattice parameters only differing by 0.1%, and an almost 2% increase in the specific volume. The volume thermal expansion coefficient was found to be  $7 \times 10^{-5} \text{ K}^{-1}$  based on variable temperature XRD measurements. This is also surprising as filling with

polyethylene has the effect of changing the sign of the thermal expansion coefficient of orthorhombic silicalite from a negative [8, 9] to a normal positive value, which is close to twice that of quartz and one order of magnitude lower than that of ultra high molecular weight pure polyethylene. It is clear that a zero thermal expansion composite could be obtained by polymerizing the appropriate amount of  $C_2H_4$  in the channels of silicalite, which in turn would lead to very interesting applications in mechanics.



**Figure 5.** EOS of PESIL: relative volume data (dots) vs.  $P$ . A third order Birch-Murnagham EOS with a  $B_0$  value of 26.7(2.0) GPa and the first derivative ( $B_0'$ ) of 4 has been fitted to the experimental points.

The equation of state (EOS) of PESIL (figure 5) along with a test of resistance against PIA were obtained by measuring powder XRD patterns as a function of pressure, up to 24 GPa, at room temperature [22]. Indeed, the Bragg peaks are clearly observed up to the maximum pressure, thereby showing that PIA of the host silicalite, which occurs progressively in pure silicalite and is complete at about 8 GPa, is prevented by the encapsulated polyethylene, which is similar to what is also observed with  $CO_2$  and Ar as guest species. An accurate EOS is obtained between ambient pressure and 6 GPa; at higher pressures PESIL is affected by strong metastabilities, which are probably due to the non hydrostatic compression in the surrounding bulk polyethylene material. Silicalite-1-F is highly compressible, with a bulk modulus ( $B_0$ ) of 13.6 GPa [12]. P-V data for PESIL can be fitted to a third order Birch-Murnagham EOS with a  $B_0$  value of 26.7(2.0) GPa and the first derivative ( $B_0'$ ) of 4. The encapsulated polyethylene in PESIL thus remarkably increases the bulk modulus to a value, which tends to approach that  $\alpha$ -quartz [26] as in the case of silicalite filled by  $CO_2$  and Ar. In addition, the density of PESIL is 2.054 (1) g/cm<sup>3</sup>, which is lower than that of  $\alpha$ -quartz by about 22%, mainly because it is a  $SiO_2/C_nH_{2n}$  composite material. An entire family of nano-composites with bulk modulus values ranging between that of pure silicalite and that of PESIL could be obtained by polymerizing a proper amount of ethylene in the channels of silicalite.

## 5. Conclusions

We have shown that application of high pressures, sometimes combined with suitable light irradiation, is a powerful, physical route for the synthesis of zeolite based nano-composite materials, where confined simple molecules either react with the internal nano-walls of the silicalite pores (silicon carbonate) or they react each other forming encapsulated polymers (PESIL). These composites have interesting physical properties. We now think that even conductive polymers could be synthesized in zeolites by similar methods, leading to nano-composites with unrivalled electrical and photonic properties. In

addition, the large volume scale up of this high pressures synthesis to 1-2 cm<sup>-3</sup> sample materials should be possible, since the pressures involved are not very high (a few Kbar or a few GPa in some cases).

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