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High Pressure and Chemical Bonding in Materials Chemistry

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

Materials chemistry under high pressures is an important research area opening new routes for stabilizing novel materials or original structures with different compositions (oxides, oxoborates, nitrides, nitridophosphates, sulfides,...).

Due to the varieties of chemical compositions and structures involved, high pressure technology is also an important tool for improving the investigations on chemical bonding and consequently the induced physico-chemical properties.

Two different approaches can be described: (i) the chemical bond is pre-existing and in such a case, high pressures lead to structural transformations, (ii) the chemical bond does not exist and high pressures are able to help the synthesis of novel materials. In both cases the condensation effect ($\Delta V < 0$ between precursors and the final product) is the general rule. In addition, through the improvement of the reactivity, high pressures can lead to materials that are not reachable through other chemical routes.

Key words: Materials Chemistry, High Pressure Synthesis, Structural Transformations, Novel Materials, Chemical Bonding

Introduction

A chemical bond can be characterized by different factors:

(i) The involved atoms, *versus* their position in the Periodic Table, inducing some specific atomic properties: electronegativity, ionization potential... and consequently the distribution of bonding electrons (leading to ionic, covalent, metallic character).

(ii) Its strength induced by the overlap of the corresponding orbitals and directly dependent on the interatomic distance, such a distance being correlated, in particular: with (a) the size of the corresponding atoms, (b) the structure of the material (inducing the coordination number), (c) the formal oxidation state of the involved cation...

The energy of the resulting chemical bond is dependent on both factors. If we compare this energy to that conveyed by high pressures, it appears that pressure is a soft thermodynamical parameter, in particular when the liquid or solid phases are concerned (Table 1).

Two different approaches can be analyzed:

Table 1. Energy added by compression *versus* the nature of the medium compared to the average energy of a chemical reaction [R. H. Wentorf, Jr. Chemical Engineering, Oct. 16, p. 177 – 186 (1961)].

Pressure (bar)	Medium	Energy cal/mol
1000	gas	3000
1000	solid	1
10 000	solid	5
100 000	iron	20
100 000	H_2O	1000
1	chemical reaction	20 000

(i) the chemical bond exists in the involved material-keeping the same chemical composition – and consequently high pressures can, through a structural transformation, modify such a bond,

(ii) the chemical bond does not exist and, in such a case, high pressure can be developed for bonding atoms, leading to the synthesis of novel materials.

Structural Transformations under High Pressures

The general factor characterizing a structural transformation (from two different structural forms: F_1 to

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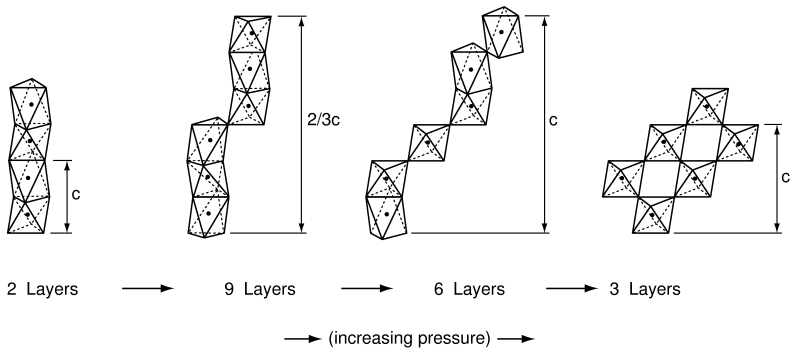

Fig. 1. Structural evolution *vs.* pressure for some ABO_3 polytypes [3].

F_2) under high pressures for a material with a constant composition (F: corresponding to a specific structural form) is the densification effect (negative ΔV value), if

$$\Delta V = \left(\frac{V_1}{Z_1}\right)_{F_1} - \left(\frac{V_2}{Z_2}\right)_{F_2}.$$

Such a structural transformation $(F_1 \rightarrow F_2)$ can be initiated by different factors: electrostatic and/or steric interactions induced through the compression of the chemical bond.

A structural transformation $(F_1 \rightarrow F_2)$ can lead to different structural phenomena:

- the removal of the charged atoms (cations or sometime anions),
- the increase of the coordination number for the most charged atoms.

Structural transformations associated with electrostatic interactions

The most illustrative example is the sequence of structural forms for the hexagonal perovskites ABX_3 from the 2H structure to the cubic 3C ones (Fig. 1) [1–3].

In such a case, the coordination number of the B^{n+} most charged cations remains constant (VI), the electrostatic repulsions B^{n+}—B^{n+} inducing the transition from face sharing octahedra (BX_6) to corner sharing ones. Consequently the B^{n+}—B^{n+} distance is increased from a d value to approximately $d\sqrt{2}$ reducing electrostatic repulsions. With the increase of the pressure the number of corner sharing (BX_6) octahedra increases.

For the $Li_2M^{4+}F_6$ fluorides (M^{4+} = Ge, Ti, Zr), structural transformations are induced by both steric and electrostatic interactions. The M^{4+}—M^{4+} distance remains approximately constant but the number of

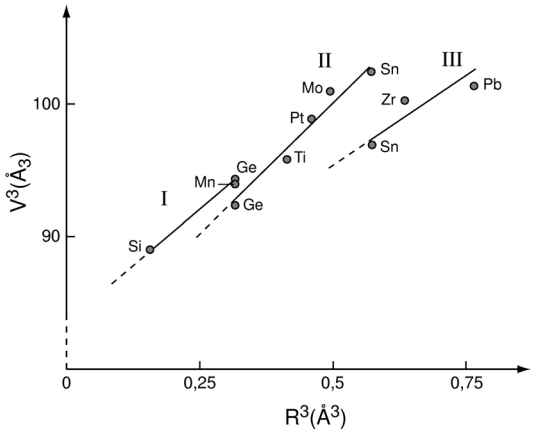

Fig. 2. Variation of the volume for a unit Li_2MF_6 *versus* $r^3(M^{4+})$ (r being the ionic radius) [4].

common edges between $(M^{4+}F_6)$ and (Li^+F_6) octahedra decreases with the M^{4+} size or under high pressures for a constant M^{4+} cation (Fig. 2) [4].

Binary oxides MO_2 at normal pressure, involving highly electropositive transition metals, are ionic and adopt 3D structures such as the rutile structure in order to minimize the electrostatic repulsion between O^{2-} anions. For example, TiO_2 adopts only the 3D rutile structure due to the large electronegativity difference between Ti and O (1.54 and 3.44, respectively). On the contrary PtO_2 – due to the smaller electronegativity difference between Pt and O (2.28 and 3.44, respectively) – can adopt at ambient pressure the layered CdI_2-type structure (α-PtO_2) [5]. Under high pressure conditions – due to the enhancement of the electrostatic repulsion – the α-PtO_2 (CdI_2-type) is transformed to the rutile form (β-PtO_2) [6]. First principles electronic calculations have recently confirmed the relative stabilities of the rutile and CdI_2 structural types *versus* the metal-oxygen and oxygen-oxygen orbital, interactions [7].

For the binary oxides characterized at normal pressure by the rutile structure, under high pressures a competition is observed between the fluorite structure (CaF_2-type, space group $Fm\bar{3}m$) and the pyrite structure (FeS_2-type, space group $Pa\bar{3}$). The transition rutile → fluorite is observed for TiO_2 [8], ZrO_2 [9] or HfO_2 [10]. On the other hand, the transition rutile → pyrite is induced for GeO_2 [11], SnO_2 [12], PbO_2 [13] and RuO_2 [13].

The main difference between both structural types being the positions of the oxygen atoms, consequently electrostatic interactions induced under high pressures appear to play a key role.

Another interesting high pressure transformation under high pressures is the transition observed for the K_2MO_3 oxides (M = Zr, Hf, Sn, Pb) from the prismatic K^+ coordination to a pseudo-octahedral one in order to reduce the $O^{-\delta}$-$O^{-\delta}$ electrostatic interactions [14].

Structural transformations are particularly interesting when different chemical bonds are involved. As an example, binary alkaline earth subnitrides $(AE)_2N$ (M = Ca, Sr, Ba) can be characterized by a unique combination of ionic and metallic bonding within the same crystal structure. Due to the formal description resulting of the charge neutrality, such a structure can be described by the formula $(AE)_2^{2+}$ -$N^{3-} \cdot e^-$. The *anti*-$CdCl_2$ structure type is built from two-dimensional hexagonal double layers of AE^{2+} atoms with nitrogen atoms centering M_6 octahedra within the layers [15]. Ionic bonding between $(AE)^{2+}$ and N^{3-} holds the $(AE)_2N$ layers together, metallic inter-layer bonding results from nearly-free remaining electrons. Under high pressures – up to 40 GPa – different phase-transitions are observed that allow to study the behaviour of this combination of chemical bonding [15].

Structural transformations induced by different bond compressibilities

The bond compressibilities allow to induce high-pressure structural transformations [16]. The development of high T_c superconductivity has improved the synthesis of a large variety of compositions and structures for complex copper oxides with different linkages of square planar CuO_4 units (1D, 2D, 3D) versus the involved counter-cation [17].

Due to the difference of compressibility between the Cu-O bond and the (counter-cation) – O bond, the structure of cuprates can be modified *versus* temperature and pressure [18]. For example the quasi-1D structure of $SrCuO_2$ (characterized by double Cu-O chains) can be transformed to a 2D-structure (with CuO_2 sheets) at 3 GPa and 900 °C [19].

The high-pressure behaviour of the $GdFeO_3$-type orthorhombic perovskites (ABO_3) – in particular the tilting of the (BO_6) octahedra – has recently been explained in terms of relative compressibilities of the (BO_6) and (AO_{12}) polyhedra. If the (BO_6) octahedra are less compressible than the (AO_{12}) dodecahedra the structural distortion is increased under high pressures. In the opposite case, if the (BO_6) octahedra are more compressible than the (AO_{12}) polyhedra; the structural distortion is decreased. A bond-valence concept has recently been developed for explaining the relative compressibilities of the cationic sites in oxide perovskites [20].

Synthesis of Novel Materials Induced by High Pressures

The syntheses helped by high pressures are also governed by a so-called "densification effect". In such a case, the negative value ΔV characterizes the difference between the volume of the precursors and that of the resulting materials [if $A + B \rightarrow AB$, $\Delta V = (V_A/Z_A + V_B/Z_B) - (V_{AB}/Z_{AB})$].

Densification effects can play an important role in phase diagrams; the formation of specific compositions different than that observed at normal pressure can be induced.

For example, in the Al_2O_3-B_2O_3 diagram, at normal pressure two compositions are observed: $9Al_2O_3$-$2B_2O_3$ and $2Al_2O_3$-B_2O_3; on the contrary at 4 GPa and the same temperature domain, the previous compositions do not exist but two new ones are stabilized (Al_3BO_6 and $AlBO_3$) [21].

In addition, different factors can induce synthesis under high pressures:

- thermodynamical factors,
- improvement of the reactivity and/or the decrease of the inter-atomic distances,
- structural factors involving the "*in-situ*" compressibility of the corresponding atoms.

Modification of the thermodynamic properties and the high pressure applications in metallurgy

Melt-quenching under high pressures has been developed in metallurgy. Through the induced thermo-

dynamical effects, high pressure processes have been mainly investigated in three domains:

- the synthesis of new alloy compositions,
- the stabilization of amorphous alloys,
- the preparation of nanostructured alloys.

Synthesis of new alloys and intermetallic compounds

The variation of melting point with pressure has been applied to improve the rapid solidification of melted alloys [22, 23].

The liquid → solid transformation is usually accompanied by a volume change. Consequently high pressures favour only the denser phases characterized by a negative ΔV value [24].

Pressure is able to have also a strong influence on the thermodynamic driving force and nucleation rate for each phase [25]. In addition, the long range atomic rearrangement will be depressed at high pressures leading to a change of the microstructure and phase composition for solidification products [26, 27].

As an illustration, high pressure has a strong influence on the solidification of Al-Mn alloys leading to a new orthorhombic $Al_{3.4}Mn$ phase as well as nanocrystalline Al obtained by quenching the Al(20 wt%) Mn alloy melt at 6 GPa [28].

In the system Ca-Au at ambient pressure, the formation of two intermetallic phases $CaAu_3$ [29] and Ca_2Au_7 [30] has been observed. Using Ca_3N_2 and metallic Au as precursors at 850 °C and a mild pressure (7.5 MPa), a new composition Ca_3Au_4 was stabilized [31].

More recently a novel intermetallic compound MgCu with a CsCl-type structure has been obtained under high pressures (6 GPa, 800 °C, 8 h.). This compound decomposes at 520 K in normal pressure conditions into Mg_2Cu and $MgCu_2$ [32].

Synthesis of amorphous alloys

Using high pressures – suppressing the diffusion processes and lowering the critical cooling rate of the amorphous formation – metallic glasses can be induced at a relatively lower cooling rate [33].

The $Cu_{85}Sn_{15}$ amorphous alloy has been prepared by melting the alloy under high pressure and cooling to r. t. at a cooling rate close to 10^3 K/s [34].

During the last twenty years the synthesis of amorphous alloys has been investigated [35, 36].

Table 2. Some illustrations of the high-pressure synthesis of novel materials from thermally unstable precursors.

Thermally unstable Precursors	Resulting materials	References
PbO_2	$PbSnO_3$	[40]
CrO_2	$PbCrO_3$	[41]
	$CaCrO_3$	[42]
HgO	Hg_xWO_3	[43]
	$Hg_2M_2O_7$	[44]

Preparation of nanocrystalline alloys

The preparation of nanocrystalline materials is strongly correlated to the control of nucleation and growth of grains. In order to prepare nanometer scaled crystals the nucleation must be strongly improved and the growth rate reduced. Due to the high pressure effects on the activation energy of viscous flow, melting rate increases and growth rate decreases.

If the pressure is high enough the grain size can be controlled by adjusting the pressure value. Nanocrystalline Zn with a grain size close to 20 nm has been prepared by high pressure melt quenching [37].

The effect of high pressures on the preparation of bulk nanocrystalline materials has also been, observed for the ternary system Pd-Si-Cu [38] and the binary system Ti-Cu [39].

Thermodynamic effects and the stabilization of thermally unstable precursors

In a chemical system, at the temperature required for the reaction between the precursors, high vapour pressure can be induced due to different thermal phenomena involving the precursors (decomposition, sublimation...). High pressures being able to suppress or to push to higher temperatures such effects, this technique is efficient for synthesizing novel materials with an appropriate stoichiometry. High pressure has been used for improving Materials Chemistry not only for preparing new oxides (Table 2) [40 – 44], but also for developing new research domains.

As an example, due to the reduced thermal stability of P_3N_5, leading to the irreversible elimination of N_2, high pressures increased the decomposition temperature leading to the synthesis of new materials from this precursor. Consequently original high pressures-high temperatures routes (4 GPa, 1300 °C) have been developed for preparing alkali and alkaline-earth nitridophosphates: $M^{I}P_4N_7$ (M = Na, K, Rb, Cs) or $M^{I}{}_3P_6N_{11}$ (M = Rb, Cs) using phosphorus nitride P_3N_5 and metal azides as precursors [45, 46].

In order to improve Materials Chemistry involving nitridophosphate, the same chemical route ($2P_3N_5 + 3Ba(N_3)_2 \rightarrow 3BaP_2N_4 + 8N_2$) has been set-up (8 GPa, 1400 °C) [47]. The crystal structure of the resulting material (BaP_2N_4) is isostructural with that of $BaGa_2S_4$ [48] and the high pressure form of CaB_2O_4 [49].

In parallel, the thermal stabilization of P_3N_5 has allowed to prepare a new high pressure form γP_2N_5 characterized by tetrahedral (PN_4) and square pyramidal (PN_5) units [50] compared to α-P_3N_5 characterized only by (PN_4) tetrahedra [51, 52]. Consequently high pressure is also able to increase the phosphorus coordination number (IV $\rightarrow$ V) and also the density (32%). Such a high pressure transformation is comparable to the stabilization of the cubic γ-Si_3N_4 phase under high pressure conditions [53, 54].

Another illustration of the development of a new high pressure chemistry is the stabilization of thioborate compounds. CaB_2S_4 has been prepared under high pressure conditions (6.2 GPa, 800 – 1100 °C) under the vapour pressure of sulphur in the required temperature domain for the reaction. In addition to the thermal stabilization of the precursors, the densification effects leads to a structure characterized by a three-dimensional linkage of (BS_4) tetrahedra and icosahedral sulphur coordination for calcium [55].

Consequently it appears that high pressures are a fruitful tool for opening new research areas in Materials Chemistry (as: nitrodophosphates, thioborates, high pressure-forms of borates...) improving the knowledge of the correlations between the chemical bond, the structure and the resulting physical properties.

Synthesis of materials with mixed anions

The preparation of materials with mixed anions requires, in most cases, the use of precursors characterized by different physico-chemical properties. Consequently the reactivity is different and high pressures can be an important tool.

During the last thirty years several new materials have been stabilized, mainly in the domain of oxyfluorides, as MOF with M = Ti, V, In [56, 57], Tl_2OF_2 [58], and $KTiO_2F$ [59].

More recently a strong interest has been devoted to nitride-halides: MNX with M = Zr, Hf and X = Cl, Br [60] or ZrNF [61].

Two different routes can be developed for preparing such materials:

- the reaction between two different precursors as: $KF + TiO_2 \rightarrow KTiO_2F$ [59],
- the use of a reactive pressure, as for the preparation of Tl_2OF_2 resulting from the treatment of TlF under oxygen pressure [58] or ZrNF obtained through a high pressure reaction of ZrN with NH_4F as source of fluorine [61].

Stabilization of strong covalent bonds under high pressure conditions

The covalency of a chemical bond is strongly correlated to the overlap of the atomic orbitals and consequently to the interatomic distance between the involved atoms.

High pressures are able to play an important role in the formation of covalent bonds through two different routes:

(i) the improvement of reactivity for the synthesis of materials with light elements (in particular the elements involving 2p orbitals: B, C, N, ...),

(ii) the stabilization of the highest oxidation states of transition metals.

Stabilization of materials with light elements

The corresponding materials involve mainly the 2p elements (B, C, N). Due to the small reactivity of such elements and the three dimensional structure of the materials characterized by a large panel of physico-chemical properties (diamond, c-BN), high pressures are required for preparing novel materials with light elements [62 – 64]. More recently the high pressure polymerisation of fullerenes has been investigated [65 – 66].

During the last ten years a strong interest for such materials has been developed with the attempts to synthesize carbonitrides – in particular 3D forms of C_3N_4 – with properties comparable with that of diamond [67 – 68]. This area can be considered as an example where computational chemistry and high pressure synthesis are associated for developing Materials Chemistry [69].

Concerning 3p elements, high pressures have recently opened new developments in silicon clathrate physical chemistry [70 – 71].

The development of novel materials with light elements will be of a great interest in the near future either for improving basic science (how chemical bonding with these elements can develop correlations be-

Table 3. Evolution of the Fe^{n+}-O distances versus the formal $n+$ value [r(Fe^{n+}) is defined on the basis of r(O^{2-}) = 1.40 Å] [72].

	Fe(III)-O ($LiFeO_2$)	Fe(IV)-O ($Sr_{0.50}La_{1.50}Li_{0.50}Fe_{0.50}O_4$)	Fe(V)-O (La_2LiFeO_6)
Fe^{n+}-O (Å)	2.03	1.95_6	1.86
r(Fe^{n+}) (Å)	0.63	0.55_6	0.46

tween Materials Chemistry and Physics) or industrial applications involving large band-gap materials, high mechanical properties, high thermal conductivity, ...

Preparation of materials with high oxidation states of transition metals

When the formal oxidation state of a metal is increased, the interatomic distance $M^{\underline{n+}}$–X is strongly reduced compared to the compressibility effect. Table 3 gives an illustration for the evolution of $Fe^{\underline{n+}}$–O distances (octahedral Fe^{n+} coordination) *versus* the improvement of the formal n+ oxidation state [72].

Due to the corresponding enhancement of the $M^{\underline{n+}}$–O bond strength, different electronic phenomena case be induced:

- intra-atomic phenomena, as the change of electronic configurations correlated to the local (Dq/B) value [73],
- inter-atomic phenomena as insulator → metal transitions [74] or – in the case of anisotropic electronic configuration [as high-spin $Fe^{4+}(t_{2g}^3 e_g^1)$ or low-spin $Ni^{3+}(t_{2g}^6 e_g^1)$] – disproportionation ($2M^{n+} \Leftrightarrow M^{(n-\varepsilon)+} + M^{(n+\varepsilon)+}$) [75, 76].

The development of such a research area appears important for improving the knowledge of correlations between the strongest chemical bonds and the induced physical phenomena.

Recently Mössbauer spectroscopy, as a local physical characterization, has allowed to follow such electronic phenomena in *RE*NiO_3 (*RE* = rare-earth) slighly doped with ^{57}Fe (1 – 2%) [77, 78].

High pressures and reactivity

The improvement of the reactivity plays an important role on the formation of chemical bonds and consequently on the synthesis of novel materials. In a general case, under high pressure conditions, the reaction time is considerably reduced and the reaction temperature also. Consequently such effects are able to help the development of high pressures and soft chemistry in materials synthesis.

Two approaches can be involved versus the physical state of the precursors.

(i) At the beginning of the development of Materials Chemistry under high pressures using solid precursors, the strong effect on the kinetics of materials preparation was underlined [79]. The inducing effects are not so well-known and it would be important to improve this knowledge.

(ii) The reaction between a solid phase and a liquid phase is able to improve strongly the reactivity. Different hypothesis have been postulated for explaining such an effect: dissolution-recrystallisation phenomena, improvement of the dissociation of the solvent, physico-chemical phenomena at the interface between solid/liquid phases *etc*. This domain involves both: hydrothermal synthesis with aqueous solutions [80, 81] or solvothermal reactions with non-aqueous solvents [82 – 84].

The first approach has led to the synthesis of novel materials. Two different families have recently been investigated under very high pressure ($P \geq 10$ GPa) and high temperature ($1100 \leq T \leq 1700$ °C) conditions: (i) the rare earth silicates $RE_2Si_2O_7$ [85] and (ii) the rare earth borates $RE_3B_5O_{12}$ with a crystal structure isostructural with the beryllo-silicate-mineral: semenorite [86]. In such a domain, high pressures help for the synthesis of these new oxides and stabilize novel interesting structures.

Hydrothermal and solvothermal reactions appear to be very fruitful. The overlap of different parameters: (i) chemical composition of the solvent adapted to that of the expected materials, (ii) use (simultaneously) of the two thermodynamical parameters: (pressure and temperature), are able to develop the synthesis of novel materials (in particular metal-organic frameworks with unusual units and mixed ligands) [87 – 88]. During the last ten years this domain has been developed either for preparing nanoparticles [89 – 90] or large single crystals [91 – 93] and for setting up new processes for the preparation of ceramics under mild conditions [94].

Modification of the reactivity through the atomic compressibility under high pressures

The compressibility of atoms, under very high pressure conditions, is able to modify the energy of the orbitals and consequently to change their electronic

structure. Such a compressibility depends on the position of such atoms in the Periodic Table [95].

On the basis of the compressibility of potassium and the associated modifications of the electronic configuration ($d^0s^1 \rightarrow s^0d^1$), Badding et al. have explained the synthesis of new materials K_xM (M = Ag, Ni, Pd) [96–98].

Conclusions and Perspectives for Developing High Pressure Materials Chemistry

Through the different aspects of high pressure contributions (thermodynamical and structural effects, improvement of the reactivity, ...) Materials Chemistry under High Pressures seems able to help the formation of specific chemical bonds and consequently to improve basic knowledge of correlations between composition/chemical bond/structure and the resulting physico-chemical properties. All the areas of the Materials Chemistry can be involved (intermetallic compounds, oxides fluorides, borides, carbides, nitrides, ...) but also materials with mixed anions (carbonitrides, fluoronitrides, ...) where two different chemical bonds are present in the same structure.

In particular,the research domain involving intermetallic compounds could be important either for basic research (as for example the high pressure structural transformations of lanthanoid platinum germanides [99] or ternary lanthanoid pnictides Li(AE)Pn (AE = Eu, Pn = P, As, Sb, Bi) [100]) or for preparing new materials for specific applications.

During the last five years, due to the progress in the diamond anvil cell and laser heating techniques [101], a new synthesis route in Materials Chemistry was initiated under very high pressure conditions (several ten GPa). This process was developed for the preparation of different novel materials: PtN [102], PtC [103], and Co_2N [104].

Such a route for preparing specific materials appears fruitful for the future but, due to the small energy conveyed by high pressures and taking into account that – in most cases – such synthesis involves the elements (metal+nitrogen or carbon) more or less non-reactive, a particular effort for improving the reactivity of the involved precursors – through a chemical analysis -could be important, in particular for reducing the preparation conditions.

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