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# High pressure in solid-state chemistry

Gérard Demazeau

## 1. Introduction

In solid-state chemistry, high pressures can be used in two different ways. The application of high pressures to existing materials leads to a decrease of the inter-atomic distances, such a decrease being correlated with the compressibility of the solid. On the other hand, high pressures can play an important role in the synthesis of new materials.

## 2. High-pressure effects on solids

With the decrease of inter-atomic distances enhancing electronic and steric repulsions, two important types of phenomenon can be induced:

- electronic phenomena;
- structural modifications.

### 2.1. Electronic phenomena induced by pressure

Different factors can affect such phenomena:

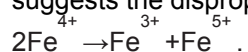
- the oxidation state  $M^{n+}$ ;
- the stability of the corresponding electronic configuration for the  $M^{n+}$  cation;
- the chemical nature of the anion;
- the inter-atomic spacing governed by the structure adopted by the solid.

Two types of electronic phenomenon can be considered:

- the intra-atomic ones—such as the change of electronic configuration in the transition from high spin (HS) to low spin (LS);
- the inter-atomic ones involving in particular: (i) charge transfer; (ii) disproportionation; and (iii) insulator  $\rightarrow$  metal transition.

Under high pressures, due to the decrease of the  $M^{n+}-X$  distance, an increase of the local crystal field energy is induced, leading to the HS  $\rightarrow$  LS transition. Such a phenomenon has been observed for  $\text{CaFeO}_3$  at a pressure close to 20 GPa [1].

The electronic behaviour of  $\text{Sr}_3\text{Fe}_2\text{O}_7$  under high pressures shows, successively, different electronic phenomena as observed using Mössbauer spectroscopy [2]. At normal pressure, the presence of two different isomer shift values suggests the disproportionation



When the pressure reaches 15 GPa, some modifications appear, suggesting a charge transfer. At  $P \geq 21$  GPa, only a single magnetic component is observed. Finally, at pressures higher than 28 GPa a metallic behaviour occurs, such a phenomenon being induced both by the strengthening of the Fe–O distance and by the instability of the HS  $\text{Fe}^{4+}$  electronic configuration ( $t_{2g}^3 e_g^1$ ). In some cases electronic phenomena such as electronic transfer can lead to the formation of a chemical bond. Such a case is observed for some metal halides such as  $\text{GeI}_4$  [3]. Under high pressures a transition is observed from a molecular state to a solid one through the formation of  $I \cdots I$  chemical bonds resulting from a decrease of Ge–I bonds, implying a charge transfer.

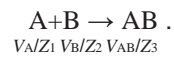
### 2.2. Structural modifications induced by pressure

Another important feature resulting from application of high pressure is the enhancement of the steric interactions between atoms throughout the whole lattice of the solid. Such interactions can lead to structural transformations. Such a phenomenon has been observed in the hexagonal  $\text{ABX}_3$  perovskites [4] and the  $\text{K}_2\text{MO}_3$  oxides (M = Zr, Hf, Sn, Pb) [5].

### 3. High pressures and the synthesis of new materials

#### 3.1. The densification effect

Due to the compressibility induced by high pressure, a densification is always observed between the starting materials and the resulting ones:



If  $V_A/Z_1 + V_B/Z_2 < V_{AB}/Z_3$  ( $\Delta V > 0$ ), high pressures hinder the formation of the resulting material AB. Otherwise ( $\Delta V < 0$ ), the application of high pressure aid the synthesis of AB.

Consequently, high pressures can modify the phase diagram. As an example, in the  $Al_2O_3$ – $B_2O_3$  system, while two compositions  $9Al_2O_3$ – $2B_2O_3$  and  $2Al_2O_3$ – $B_2O_3$  are observed at normal pressure, at 4 GPa two new phases appear:  $Al_3BO_6$  and  $AlBO_3$  [6], due to their denser structures.

**Table 1.** Fe, Lo, Ni, Cu: unusual oxidation states of transition metals stabilized under high oxygen pressures.

Iron	Cobalt
<b>Fe<sup>4+</sup></b>	<b>Co<sup>3+</sup></b>
CaFeO <sub>3</sub> [14]	TCoO <sub>3</sub> [19]
SrFeO <sub>3</sub> [15]	SrTCoO <sub>4</sub> [20]
A <sub>0.50</sub> La <sub>1.5</sub> (Li <sub>0.50</sub> Fe <sub>0.50</sub> )O <sub>4</sub> [16]	
(SrLa)(M <sub>0.50</sub> Fe <sub>0.50</sub> )O <sub>4</sub> [17]	
<b>Fe<sup>5+</sup></b>	<b>Co<sup>4+</sup></b>
La <sub>2</sub> LiFeO <sub>6</sub> [18]	Sr <sub>0.50</sub> La <sub>1.5</sub> Li <sub>0.50</sub> Co <sub>0.50</sub> O <sub>4</sub> [21]
Nickel	Copper
<b>Ni<sup>3+</sup></b>	<b>Cu<sup>3+</sup></b>
TNiO <sub>3</sub> [22]	LaCuO <sub>3</sub> [24]
SrTNiO <sub>4</sub> [23]	La <sub>2</sub> Li <sub>0.50</sub> Cu <sub>0.50</sub> O <sub>4</sub> [25]
	SrLaCuO <sub>4</sub> [26]

#### 3.2. The stabilization of the precursors

Two different systems can be considered: (i) where the precursors are thermally unstable; and (ii) where the physico-chemical properties of the precursors are so different that the chemical reaction is difficult. In both cases, high pressures can make possible the synthesis of new materials.

It is difficult to improve the chemical reaction using different anionic systems but under high pressures, an oxyfluoride  $KTiO_2F$  with the perovskite structure has been stabilized [7]. Consequently new mixed anionic compounds could be prepared in the near future: (O, F), (O, N), (N, F), ... [8].

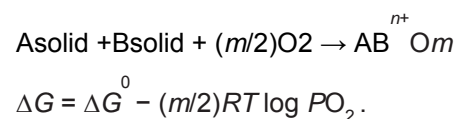
When one of the precursors is thermally unstable, the decomposition temperature ( $T_D$ ) being lower than the reaction ones ( $T_R$ ), high pressures—through the increase of  $T_D$  ( $T_D > T_R$ )—can facilitate the chemical reaction. Such applications of high pressure have been developed for preparing new compounds using HgO [9], MnO<sub>2</sub> [10], PbO<sub>2</sub> [11] as precursors.

#### 3.3. Synthesis of new compositions through the difference in atomic compressibility

The structure adopted by materials is closely related to the ratio of the sizes of the atomic species. For example, the stability of the pyrochlore structure  $A_2B_2O_7$  is limited by  $r_A/r_B \approx 1.55$  [22]. Under high pressures, this limit can be pushed to 1.8 for the series  $T^{3+}_2Ge^{4+}_2O_7$  due to the difference in compressibility between  $T^{3+}$  (T = rare earth) and  $Ge^{4+}$  [13].

#### 3.4. Stabilization of the highest valence states of transition metals under high oxygen pressures

High oxygen pressures have been developed in gas, liquid, and solid phases [14] and can help in the stabilization of the highest oxidation states of transition elements:



During the last 30 years a lot of unusual valencies have been stabilized in oxygen lattices mainly derived from the perovskite structure (table 1).

### 3.5. Synthesis of superhard materials

The physico-chemical properties (in particular hardness) of materials depend on different factors, in particular:

- the inter-atomic distance;
- the ionicity coefficient;
- the structure adopted (2D or 3D).

Consequently, materials containing light elements such as B, C, N, O could be worth investigating for the production of superhard materials [29] in view of the small atomic spacing  $d$ . The first materials found to have exceptional properties were diamond [30, 31] and, subsequently, cubic BN [32].

The evaluation of the  $B$ -modulus through an empirical formula ( $B = (1971 - 220\lambda)/d^{3.5}$ ) [33] has the development of improved high pressures for preparing new materials with light elements. Five different research areas have been investigated and could involve high pressures:

- the polymerization of fullerenes [34, 35];
- the B–C–N system [36]–[38];
- the B–O system [39, 40];
- the stabilization of carbonitrides, in particular C<sub>3</sub>N<sub>4</sub> [41, 42];
- the Si–C–N system [43].

### 3.6. The development of solvothermal reactions

A solvothermal reaction can be described as a reaction in a closed system in the presence of a solvent in supercritical conditions, or near such conditions; consequently high pressures can be involved.

Due to the specific properties of solvents in these conditions, solvothermal reactions improve the reactivity [44].

These reactions have been used in different areas:

- the synthesis of new materials (for example the phyllosiloxides—bidimensional oxides isostructural to the phyllosilicates [45]);
- the preparation of the graphitic form of C<sub>3</sub>N<sub>4</sub> [46];
- the development of new processes, such as the solvothermal preparation of c-BN [47] at lower  $P$ ,  $T$  than previously;
- the shaping of materials (sintering at low temperatures [44] or the preparation of microcrystallites [48]).

## 4. Conclusions

During the last 50 years, high pressures have been used fruitfully in solid-state chemistry as a tool for studying the physico-chemical properties of materials in extreme conditions, for stabilizing new materials able to help in improving our basic knowledge of the solid state, and to lead to functional properties for industrial applications.

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