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Materials Chemistry under High Pressures – Some Recent Aspects

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Among the thermodynamic parameters governing the preparation of novel materials, temperature \((T)\) and pressure \((p)\) play an important role. In Materials Chemistry, the synthesis of materials needs energy in order to enhance the diffusion of atoms to the equilibrium positions required by the specific structure and to induce the formation of chemical bonds. The comparison of the energy conveyed by both parameters \((p\) and \(T)\) underlines that high pressures can be associated – in liquid or solid media – with soft processes. Consequently this paper describes the main factors induced by the parameter pressure that are able to support new structural forms or generate novel materials. Two different approaches are presented: (i) for a given composition with characteristic chemical bonds, high pressures can induce structural transformations, (ii) starting from different precursors – which do not react under ambient pressure conditions – high pressures can induce the formation of new chemical bonds to give novel materials.

**Key words:** Materials Chemistry, High-pressure Phases

**Introduction**

Pressure and temperature, as thermodynamic parameters, play an important role in the preparation of novel materials. For materials synthesis involving the formation of chemical bonds it is necessary in a first step to compare the energy developed by high pressures to the average value of the energy of chemical bonds. Table 1 gives a comparison of the energy conveyed by pressure in different media (gas, liquid, solid) and the average energy of a chemical bond [1].

If the temperature reached during the materials synthesis is mainly determining atomic diffusion, due to the small energy conveyed by pressure, what are the effects of this second thermodynamic parameter in Materials Chemistry? In a first analysis, high pressures can become involved through two different approaches [2]:

(i) \(p\) and \(T\)

(ii) \(p\) and \(T\)

**Structural Transformations Induced by High Pressures**

What are the main factors inducing structural transformations under high-pressure conditions? Broadly we can distinguish three main factors:

(i) the densification effect correlated to the decrease of the lattice volume under pressure,

(ii) the improvement of electrostatic interactions (if the coordination number remains constant) due to...
Fig. 1. Scheme for the structural evolution vs. pressure for some ABO$_3$ polytypes. Increasing pressure shifts the structure from left to right.

Table 1. Energy added by compression versus the nature of the medium compared to the average energy of a chemical reaction [1].

<table>
<thead>
<tr>
<th>Pressure (bar)</th>
<th>Medium</th>
<th>Energy cal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>Gas</td>
<td>3000</td>
</tr>
<tr>
<td>1000</td>
<td>Solid</td>
<td>1</td>
</tr>
<tr>
<td>10 000</td>
<td>Solid</td>
<td>5</td>
</tr>
<tr>
<td>100 000</td>
<td>Iron</td>
<td>20</td>
</tr>
<tr>
<td>100 000</td>
<td>H$_2$O</td>
<td>1000</td>
</tr>
<tr>
<td>1</td>
<td>Chemical reaction</td>
<td>20 000</td>
</tr>
</tbody>
</table>

Structural transformations involving the “densification effect”

Considering a structural transformation induced by pressure from $F_1$ to $F_2$ ($F$ being a structural form), due to the compressibility the $\Delta V$ value between the two forms is negative:

$$\Delta V = \sum (V/Z)_{F_2} - (V/Z)_{F_1}$$

(where $V$ is the unit cell volume and $Z$ is the number of formula units per unit cell).

Under high pressures only structural transformations characterized by a negative $\Delta V$ value can take place. This factor has been used for preparing new structural forms as well as novel materials. The increase in pressure during the synthesis leads to a more dense structure than that observed under normal conditions. To give an example, the high-pressure $TV_2O_6$ phases ($T = Ni, Mg, Co, Zn, Mn, Cd$) with the orthorhombic columbite structure differ from the brannerite-type structure observed for normal-pressure conditions [3]. This phenomenon has also been used for the stabilization of Laves phases (MgCu$_2$-type) such as LaCo$_2$ or $REFe_2$ ($RE = Pr, Nd, Yb$) [4, 5].

Structural transformations through electrostatic interactions

One of the main effects associated with the application of high pressures to a solid phase is the decrease of the average distances between atoms participating in the involved structures. For ionic/covalent materials, the electrostatic repulsion between the most highly charged cations or anions is increased ($q q' / d^2$), thus causing instability. In order to reduce these adverse effects, the structure is changes to another one involving higher coordination numbers of the atoms often associated with larger interatomic distances (the “pressure-coordination rule” and the “pressure-distance paradox”).

A well known illustration of this type of structural transformation is the evolution of the structure versus increasing pressure of the hexagonal perovskites ABX$_3$: from the 2H structure (where only shared faces are involved) to the 3C structure (characterized only by shared corners) (Fig. 1). Between these two extreme forms, through the continuous transformation from shared faces to shared corners versus pressure, different structures can be stabilized [6].

Structural transformations induced by different compressibilities of the involved chemical bonds

The structure of a specific material is mainly induced by the number of anions coordinated to cations
involved. Considering that the cation coordination is correlated to the cation-anion distance (C–A), modification of such cation-anion distances for different cations C₁, C₂, . . . can induce new structures.

**Structural transformations of rare earth platinum stannides REPtSn**

A recent example for such a behaviour is the structural transformation observed for the REPtSn stannides (RE = La, Ce, Pr, Nd, Sm). With the light rare earth metals (which are the largest due to the lanthanoid contraction) (La, Ce, Pr, Nd, Sm, Eu), the REPtSn stannides adopt the TiNiSi-type structure (Z = 4); on the contrary, for the smaller rare earth metals (Gd – Lu) they adopt the ZrNiAl-type (Z = 3) [7, 8].

At normal pressure the compound CePtSn adopts the TiNiSi-type structure but under high pressures (9 – 10 GPa and 1050 °C) the ZrNiAl structure is stabilized (Fig. 2) [9]. Such a structural transformation corresponding to a reconstructive phase transition is characterized by a negative $\Delta V$ value:

\[
\left[ \frac{V}{Z(\text{HP–CePtSn})} - \frac{V}{Z(\text{NP–CePtSn})} \right] = 68.7 \text{ Å}^3 - 69.3 \text{ Å}^3 = -0.6 \text{ Å}^3,
\]

which is less than 1% of the average volume.

The most evident difference between the two structural modifications (the NP and the HP forms) concerns the cerium coordination, *i.e.* $d$(Ce–Ce) NP–CePtSn $\sim$ 4.12 Å and $d$(Ce–Ce) HP–CePtSn $\sim$ 4.02 Å. Thus we observe a significant reduction during this high-pressure structure transformation. Due to the electronic structure of the rare earth elements (filling of 4$f$ orbitals) the compressibility of the cerium atoms as compared to the Pt and Sn atoms (filling of $d$ or $p$ orbitals) is more pronounced leading to a slightly smaller radius in the high-pressure modification.

**Structural transformations of SrCuO$_2$**

Due to the difference in compressibility between the Cu–O bond and the (counter-cation)–O bond (Sr–O bond in this case), the structures of various cuprates can be changed *versus* pressure and temperature. For example the quasi-1D structure of SrCuO$_2$, characterized by Cu–O double chains, is transformed to a 2D structure with (CuO$_2$) sheets at 3 GPa and 900 °C [10].

**Synthesis of Novel Materials Induced by High Pressures**

When the target chemical bonds do not already exist in the precursors, then high pressures allow the synthesis of novel materials [11 – 13]. Broadly the synthesis of novel materials under high-pressure conditions depends on two sets of parameters:

(i) the thermodynamical effects associated with the specificities of the pressure parameter,

(ii) the chemical effects mainly associated with the enhancement of the reactivity of the precursors.
The thermodynamic effects associated with the specificities of the pressure parameter

In a first approximation, three main effects can be considered:

(i) the "Le Chatelier’s rule" reducing the formation of gas or liquid phases,
(ii) the densification – as a specific case of “Le Chatelier’s rule” – leading to a negative $\Delta V$ value,
(iii) the compression of the involved atoms and its correlation with the resulting structure.

Le Chatelier’s rule and the synthesis of novel materials

In order to maintain the stoichiometry, it is necessary to prevent any modification of the chemical composition of the reactants in the temperature domain required for the synthesis. Regarding their thermal stability, different materials are decomposed at a specific temperature $T_d$. Consequently, the required pressure domain must be selected as to allow an increase of $T_d$ beyond the reaction temperature domain $T_M$. Such high-pressure processes have been extensively used since the first developments of high-pressure synthesis of novel materials [14].

High pressures can assist in the preparation of novel materials through the stabilization of thermally labile precursors. During the last 50 years, many complex oxides have been obtained in this way for which the thermal stability of the precursors (as for example: MnO$_2$, HgO, PbO$_2$, …) is increased beyond the reaction temperature [15, 16].

Synthesis of the SrCrO$_3$ perovskite

This material was first prepared under high pressures by B. Chamberland [17]. More recently, in order to investigate the physical properties of such Cr(IV) perovskites, SrCrO$_3$ was revisited, with high pressures applied for stabilizing the CrO$_2$ used as a precursor [18]. Cr(IV) is not stable owing to two decomposition pathways:

(i) thermal deoxygenation:

\[
(2 \text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3 + \frac{1}{2} \text{O}_2)
\]

(ii) Cr(IV) disproportionation:

\[
3 \text{Cr(IV)} (O_h) \rightarrow 2 \text{Cr(III)} (O_h) + 1 \text{Cr(VI)} (T_d).
\]

Fig. 3 shows the X-ray diffraction pattern of SrCrO$_3$ confirming the cubic perovskite structure. A powder neutron diffraction study (Fig. 4) of the sample was performed at 100 and 10 K at the ILL diffractometer D20. Between 100 and 10 K, a structural phase transition to $Imma$ symmetry occurs, but no magnetic peaks are evident at 10 K. The results of magnetic mea-
measurements on SrCrO \(_3\) are given in Fig. 5. Based on susceptibility measurements at only three temperatures Chamberland [17] had concluded Pauli paramagnetism for this perovskite. The recent magnetic results suggest a partial spin ordering at low temperature.

**High-pressure synthesis of a new structural form of P\(_3\)N\(_5\)**

Recently, it was possible to stabilize new forms of nitrides using high pressures. The thermal stabilization of P\(_3\)N\(_5\) has led to investigations of its structural transformations, and a new high-pressure phase, \(\gamma\)-P\(_3\)N\(_5\), was stabilized [19]. The normal-pressure and high-pressure forms are shown in Fig. 6. In contrast to the normal-pressure modification \(\alpha\)-P\(_3\)N\(_5\) [20], which is built up from corner- and edge-sharing PN\(_4\) tetrahedra, the structure of the high-pressure modification \(\gamma\)-P\(_3\)N\(_5\) is characterized by tetrahedral (PN\(_4\)) and square pyramidal (PN\(_5\)) groups [19].

This kind of transformation is comparable to the stabilization of the cubic Si\(_3\)N\(_4\) phase under high pressures. The normal-pressure \(\alpha\)- and \(\beta\)-Si\(_3\)N\(_4\) modifications contain exclusively (SiN\(_4\)) units, while the high pressure \(\gamma\)-Si\(_3\)N\(_4\) structure (spinel type) exhibits Si in two different types of coordination, *i.e.* (SiN\(_4\)) and (SiN\(_6\)) units [21, 22].

**Synthesis of novel materials through the “densification effect”**

This effect is, in most cases, accompanied by an increase of the coordination number of the anions.

**High-pressure study of the systems RE\(_2\)O\(_3\)-B\(_2\)O\(_3\)**

The chemical system RE\(_2\)O\(_3\)-B\(_2\)O\(_3\) was recently investigated under high-pressure conditions [23]. At normal pressure, three different compositions are observed: \(\text{REBO}_3\), \(\text{RE}_3\text{BO}_6\), and \(\text{REB}_3\text{O}_6\) [24]. Under high pressures, three new compositions of rare earth borates have been prepared depending on the size of the metal: \(\alpha\)-RE\(_2\)B\(_4\)O\(_9\) (with RE = Eu, Gd, Tb, Dy) [25], \(\text{RE}_4\text{B}_6\text{O}_{15}\) (with RE = Dy, Ho) [26], and \(\text{RE}_3\text{B}_5\text{O}_{12}\) (for RE = Er–Lu) [27]. If we compare the \(\Sigma V/Z\) of the precursors to the V/Z of the HP phases, in all cases the \(\Delta V\) values are negative (Table 2).

**High pressures and the stabilisation of high coordination numbers (CN)**

During the last forty years, when high pressures were used in materials synthesis, the synthesis of
novel perovskites ABO$_3$ was the most important domain [28, 29]. This development can be attributed to the high cation coordination numbers observed in such a structure: CN 12 (or CN 8 + 4 as a common distortion) for the larger cation A and CN 6 for the smaller cation B. Different illustrations can be given from recent research studies:

(i) Synthesis of the perovskites SeMO$_3$ with $M^{2+}$ = Mn, Co, Ni [30].
(ii) Synthesis of the pseudo-perovskites AA$'$$_3$B$_4$O$_{12}$ [31].
(iii) Synthesis of perovskites Sr$_3$Cr$_2$ReO$_9$ and SrCr$_2$Ru$_{1−x}$O$_3$ [18, 32].

Synthesis of the pseudo-perovskites AA$'$$_3$B$_4$O$_{12}$

The pseudo-perovskite CaCu$_3$Mn$_4$O$_{12}$ has been prepared for the first time under high-pressure conditions [36, 37]. The main characteristic of this structure is the stabilization of a transition metal with a Jahn-Teller electronic configuration in the A site (Cu$^{2+}$) (Fig. 7).

In order to improve the magnetic properties of these oxides, the Ca$^{2+}$ cation was replaced by rare earths RE$^{3+}$. The compounds RECu$_3$Mn$_4$O$_{12}$ (RE from La$^{3+}$ to Yb$^{3+}$) have thus been prepared under moderate pressure conditions ($p = 2$ GPa and $T = 1000$ $°$C) with reactive precursors and KClO$_4$ [31].

The magnetic ordering temperature for the TMO$_3$ perovskites generally decreases as the size of RE$^{3+}$ is reduced [38], but in RECu$_3$Mn$_4$O$_{12}$ perovskites, $T_C$ increases from La$^{3+}$ to Yb$^{3+}$ (Fig. 8b). This phenomenon can be attributed to the decrease of the $d$ (Mn–O) distance (Fig. 8a) leading to an improvement of the overlap of 3$d$ (Mn) and 2$p$ (O) orbitals. The interest in these perovskites arises from the observation of a substantial low-field magnetoresistance (about 2%) at room temperature, which is promoted by the electron injection effect induced upon replacement of Ca$^{2+}$ by RE$^{3+}$ [39].

Table 2. Evaluation of the $\Delta V$ values for selected high-pressure phases in the system RE$_2$O$_3$–B$_2$O$_3$.

<table>
<thead>
<tr>
<th>$\alpha$–RE$_2$B$_2$O$_5$: $\Sigma$/Z precursors (Å$^3$)</th>
<th>$\Sigma$/Z (Å$^3$)</th>
<th>$\Delta V$ = $[\Sigma$/Z($\alpha$–RE$_2$B$_2$O$_5$) – ($1\Sigma$RE$_2$O$_3$ + $2\Sigma$B$_2$O$_3$) $\Sigma$/Z (precursors)] (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eu</td>
<td>170.6</td>
<td>139.1</td>
</tr>
<tr>
<td>Gd</td>
<td>169.0</td>
<td>138.1</td>
</tr>
<tr>
<td>Dy</td>
<td>166.5</td>
<td>135.5</td>
</tr>
<tr>
<td>Ho</td>
<td>164.4</td>
<td>134.4</td>
</tr>
<tr>
<td>RE$_2$B$_2$O$_5$: $\Sigma$/Z precursors (Å$^3$)</td>
<td>$\Sigma$/Z (Å$^3$)</td>
<td>$\Delta V$ = $[\Sigma$/Z(RE$_2$B$_2$O$_5$) – ($1\Sigma$RE$_2$O$_3$ + $2\Sigma$B$_2$O$_3$) $\Sigma$/Z (precursors)] (Å$^3$)</td>
</tr>
<tr>
<td>Dy</td>
<td>287.7</td>
<td>240.0</td>
</tr>
<tr>
<td>Ho</td>
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<th>$\Sigma$/Z (Å$^3$)</th>
<th>$\Delta V$ = $[\Sigma$/Z($\alpha$–RE$_2$B$_2$O$_5$) – ($1\Sigma$RE$_2$O$_3$ + $2\Sigma$B$_2$O$_3$) $\Sigma$/Z (precursors)] (Å$^3$)</th>
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<td>164.4</td>
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<td>$\Sigma$/Z (Å$^3$)</td>
<td>$\Delta V$ = $[\Sigma$/Z(RE$_2$B$_2$O$_5$) – ($1\Sigma$RE$_2$O$_3$ + $2\Sigma$B$_2$O$_3$) $\Sigma$/Z (precursors)] (Å$^3$)</td>
</tr>
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<td>Dy</td>
<td>287.7</td>
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</tr>
<tr>
<td>Ho</td>
<td>283.8</td>
<td>238.3</td>
</tr>
</tbody>
</table>

The precursors were H$_2$SeO$_3$ and MO (M = Mn, Co, Ni, Cu, and Zn). Two main effects can explain the synthesis under high-pressure conditions. i) Pressure helps to minimize the electronic anisotropy induced by the Se “electron lone pair”, and ii) it favours the stabilization of a strongly distorted perovskite structure, characterized by a small tolerance factor (given the small size of the Se$^{4+}$ cations) and an abnormally high tilting effect of the MO$_6$ octahedra, with $M$–O–M angles of around 124–130$°$. Such an effect was also observed for a Bi$^{3+}$ perovskite (BiNi$_3$O$_5$ for which a (Bi$_{0.50}$Bi$_{0.50}$)$^{3+}$Ni$^{2+}$O$_3$ oxidation state distribution has been proposed [33, 34]). In fact, Se$^{4+}$ as a 4$s^2$ cation is too small (∼0.50 Å) to occupy the A site in the perovskite structure and the “lone pair” fills the residual space; Se$^{4+}$ is very close to 3 oxygen atoms (instead of 12) and a pyramidal selenite group SeO$_3^{2−}$ can be defined. Thus, the octahedra are highly tilted, with strongly bent M–O–M angles giving rise to both ferromagnetic and antiferromagnetic interactions [35].

Fig. 7. Structure of the pseudo-perovskite CaCu$_3$Mn$_4$O$_{12}$.
Fig. 8. Evolution of the \( d(\text{Mn–O}) \) distance in the \( \text{RECu}_3\text{Mn}_4\text{O}_{12} \) structures vs. the \( \text{RE}^{3+} \) ionic radius (8a) and the influence on the \( T_c \) value (8b).

High-pressure synthesis of double perovskites

High pressures are required in many cases for stabilizing double perovskites \( \text{A}_2\text{BB’O}_6 \) [40]. In these cases, different effects can support the synthesis: (i) the "densification effect" favoring the coordination number 6, (ii) the "in situ" increase of the electrostatic interactions helping the cationic B/B’ ordering process. Two different examples have been selected in order to illustrate the stabilization of double perovskites.

(i) Stabilization of \( \text{Sr}_3\text{Cr}_2\text{ReO}_9 \) [\( \text{Sr}(_{2/3}\text{Cr}_{2/3}\text{Re}_{1/3})\text{O}_3 \)]

The selected precursors were \( \text{SrO}, \text{Cr}_2\text{O}_3, \) and \( \text{ReO}_3 \). Under normal pressure conditions this compound is not obtained and the formation of \( \text{Cr}^{6+} \) is observed. In order to prevent the formation of \( \text{Cr}^{6+} \) through the destabilization of its tetrahedral coordination, high pressures have been used for preparing

\[ \begin{align*}
\text{Sr}_3\text{Cr}_2\text{ReO}_9 & \rightarrow \text{Sr}_2\text{Cr}_3\text{ReO}_9 + \text{Sr} \text{O} \\
& \rightarrow \text{Sr}_2\text{Cr}_4\text{ReO}_9 + \text{Sr}_2\text{ReO}_3 \\
& \rightarrow \text{Sr}_2\text{Cr}_5\text{ReO}_9 + \text{Sr}_2\text{Cr}_3\text{O}_6
\end{align*} \]

(ii) Preparation of solid solutions of \( \text{SrCrO}_3 \) and \( \text{SrRuO}_3 \)

The first attempt was the synthesis of \( \text{Sr}_2\text{CrRuO}_6 \). Three different cationic distributions can be involved: \( \text{Sr}_2\text{Cr}^{3+}\text{Ru}^{5+}\text{O}_6 \) (B-cations ordered due to the difference of charge and size), \( \text{Sr}_2\text{Cr}^{4+}\text{Ru}^{4+}\text{O}_6 \) (B-cations disordered?), or an intermediate distribution between these two [18]. The high-pressure treatment seems to favor the formation of a cation disordered perovskite. However, the volume discontinuity near \( x = 0.5 \) (Fig. 9) in the structural evolution of the \( \text{SrRu}_{1-x}\text{Cr}_x\text{O}_3 \) series suggests that some \( \text{Cr}^{4+}/\text{Ru}^{4+} \rightarrow \text{Cr}^{3+}/\text{Ru}^{5+} \) charge transfer occurs.

High-pressure synthesis of materials through the compressibility of atoms

The compressibility of an atom is modified by its electronic configuration and is thus determined by its position in the Periodic Table. High pressures have contributed to the synthesis of novel materials in two domains:

a) The stabilization of new materials regarding the modification of the \( r_A/r_B \) ratio (\( r_A \) and \( r_B \) are the ionic radii of the corresponding atoms). For example, in the
case of the \( \text{RE}_2\text{M}_2\text{O}_7 \) pyrochlore structure, the limit of stability is defined by \( \frac{r_A}{r_M} \approx 1.55 \), in spite of the \( \frac{r_A}{r_M} \) ratio being close to 1.8 under normal conditions. Due to the difference of the compressibility between rare earth \( \text{RE}^{3+} \) and Ge\(^{4+} \) it was possible to prepare the \( \text{RE}_2\text{Ge}_4\text{O}_7 \) series (\( \text{RE} = \text{rare earth} \)) with the pyrochlore structure under high-pressure conditions [41].

Another example is the preparation of the \( \text{RE}_2\text{CuO}_4 \) oxides. The \( \text{Nd}_2\text{CuO}_4 \)-type structure can be stabilized through the synthesis at ambient pressure for \( \text{RE} \) cations from Nd to Gd [42–44]. From simple geometrical considerations, the cubic eight-fold coordination of oxygen for \( \text{RE}^{3+} \) is stabilized for \( \frac{r_{\text{RE}}}{r_O} > 0.73 \). Consequently, compounds \( \text{RE}_2\text{CuO}_4 \) with \( \frac{r_{\text{RE}}}{r_O} < 0.73 \) cannot be obtained at ambient pressure. Using high-pressure conditions (6 GPa), the \( \text{RE}_2\text{CuO}_4 \) (\( \text{RE} = \text{Y}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm} \)) materials with the \( \text{Nd}_2\text{CuO}_4 \)-type structure were prepared [45]. Such a synthesis confirms again that high pressure leads to an increase in the coordination numbers in a structure [46,47].

b) The reactivity of a given element can be modified if the pressure is high enough to induce a change of the electronic population of its orbitals. To give an example, the electronic configuration of potassium under normal pressure is \( 1\text{s}^1 2\text{d}^0 \), but under very high pressure (up to 10 GPa), due to the variation of their respective energy vs. pressure, \( d \) orbitals are stabilized. Consequently, the electronic configuration becomes \( 1\text{s}^0 2\text{d}^1 \) and potassium acquires chemical properties comparable to a transition metal. This phenomenon can explain the formation of intermetallic compounds (\( \text{K}_x\text{A}_y \)) under very high pressures using diamond anvil cells [48,49].

Another recent example is the high-pressure synthesis of novel metallopurpates \( \text{T} \text{Sr}_2\text{RECu}_2\text{O}_8 \) (\( \text{T} = \text{Cr, Ir, . . .} \)). The interest in these materials arose when superconductivity (at \( \sim 30 \) K) and magnetic ordering (at \( \sim 150 \) K), two antagonistic properties, were discovered to coexist in the same material, \( \text{RuSr}_2\text{GdCu}_2\text{O}_8 \), also referred as Ru–1212, which is one of the few cuprates that can be prepared at ambient pressure. By using high-pressure/ high-temperature conditions, we demonstrated that the majority of rare earth elements can be introduced in the gadolinium site and, furthermore, the yttrium case shows the highest \( T_c \) found in this family of phases [50,51]. High pressures are also needed to replace ruthenium by other transition elements and, interestingly, chromium is stabilized in this structure as \( 4\text{d}^3 \) in octahedral coordination [52]. Iridium also may enter the structure giving rise to a novel ferrimagnetic material. The structure is shown in

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**Fig. 10.** The crystal structure of \( \text{IrSr}_2\text{GdCu}_2\text{O}_8 \). The octahedral \( \text{IrO}_6 \) and square planar \( \text{CuO}_4 \) environments are emphasized. Note that the oxygen atoms around iridium were refined with split positions. For details see [53].

**Fig. 11.** Rietveld refinement plot of the X-ray diffraction data for (1) \( \text{IrSr}_2\text{GdCu}_2\text{O}_8 \) and the two impurity phases (2) \( \text{Sr}_3\text{IrCuO}_6 \) and (3) \( \text{SrCuO}_2 \) (Figure taken from [53]).
Fig. 10 and the corresponding X-ray diffraction pattern in Fig. 11 [53].

It is notable that the pressures required to form the structure depend on the cation sizes (either on the $T$ or on the $RE$ positions) and, even more strikingly, the experimental $p$ values which are needed for a specific $T$–1212 family versus the rare earth sizes seem to follow a parabolic law, the minimum always being found for oxides with $RE =$ gadolinium.

Two hypotheses can be proposed:
(i) variation of the reactivity of the corresponding precursors or,
(ii) variation of the rare earth compressibility versus the filling of 4$f$ orbitals (Gd 4$f^7$).

Theoretical ab initio calculations are being made to understand this behaviour.

**The chemical effects mainly associated with the enhancement of the reactivity of precursors under high pressures**

Broadly three main factors play an important role in the high-pressure synthesis of novel materials:
(i) improvement of the kinetics of the chemical reactions,
(ii) improvement of the reactivity at the interface of liquid/solid phases (synthesis, crystal growth, etc.),
(iii) reactive pressure (example: stabilization of the highest oxidation states of transition metals using high oxygen pressure as a reactive gas).

**Improvement of the reactivity at the interface of liquid/solid phases**

Hydrothermal or solvothermal reactions have been developed mainly in two domains of research:
(i) the synthesis of novel materials,
(ii) the crystal growth of materials either for basic research (to reproduce the natural single crystals formed under geothermal conditions) [55] or for industrial applications ($SiO_2$–$\alpha$, $AlPO_4$, $ZnO$, GaN, . . .) [56–64].

**Synthesis of novel materials**

The development of hydrothermal (use of aqueous solutions) or solvothermal techniques (use of non-aqueous solutions) has given access to many novel materials during the last thirty years [65]. Various examples can be given, notably the synthesis of a new class of bi-dimensional oxides (the phyllosiloxides) isostructural to the natural phyllosilicates [66, 67] or the stabilization of hybrid materials between solid state chemistry and organic chemistry [68–70]. In addition, the use of non-aqueous solvents should improve the stabilization of new non-oxidic compounds (nitrides, sulfides, phosphides, . . .) in the future [71].

**The crystal growth of materials**

High-pressure crystal growth of $RENiO_3$

The perovskite series $RENiO_3$ ($RE = Y, La \rightarrow Lu$) and $TlNiO_3$ prepared under high pressures are important examples for studying electronic phenomena in solids. From $La^{3+}$ to $Lu^{3+}$, due to the decrease of the $RE^{3+}$ size, the distortion of the perovskite structure increases. Consequently, the $Ni^{3+}$–O–$Ni^{3+}$ angle is reduced from 165° for $LaNiO_3$ to 145° for $LuNiO_3$, inducing a decrease of the overlap between 3$d$(Ni$^{3+}$) and 2$p$(O$^{2-}$) orbitals. A metal $\rightarrow$ insulator transition is observed following the decrease of the $RE^{3+}$ cation size ($La \rightarrow Lu$) [72]. For the same $RE^{3+}$ cation an insulator $\rightarrow$ metal transition is also observed versus $T$ due to the gradual opening of the Ni–O–Ni angles [73].

In addition, Ni$^{3+}$ in the low spin state has an anisotropic electronic configuration which induces an electronic instability. Such instability can be ascribed to three different effects:
(i) a Jahn-Teller distortion,
(ii) an insulator $\rightarrow$ metal transition,
Fig. 12. $^{57}$Fe Mössbauer spectra of $\text{ANiO}_3$ ($\text{A} = \text{Ti, Lu, Y}$) at 300 K. For details see [75].

(iii) the disproportionation: $2\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} + \text{Ni}^{4+}$ [74]. In addition, due to the strong covalency of the $\text{Ni}^{3+}$–O bond, a partial charge transfer: $\text{Ni}^{3+} \rightarrow \text{Ni}^{2+} (\text{O}^2-)$ ($\text{L}$ representing an electronic hole at oxygen) can take place.

The $\text{RENiO}_3$ perovskites were investigated in order

a) to detect the specific electronic phenomena (in particular disproportionation) using a local probe ($^{57}$Fe Mössbauer spectroscopy),
b) to get single crystals under high pressures and thus have access to a wider range of physico-chemical characteristics.

a) Investigation of the electronic phenomena: Mössbauer characterization of $\text{Ni}^{3+}$ disproportionation in the $\text{RENiO}_3$ perovskites

Recently, using $^{57}$Fe Mössbauer spectroscopy on $^{57}$Fe doped $\text{RENiO}_3$ nickelates, two different posi-

Fig. 13. Single crystal of $\text{NdNiO}_3$ prepared through a hydrothermal process.

tions have been assigned for $^{57}$Fe (Fig. 12). This result was taken as evidence for two types of nickel positions in the $\text{RENiO}_3$ structure corresponding to two different nickel species: $\text{Ni}^{(3+)}$ and $\text{Ni}^{(3-)}$, and confirming the results obtained through neutron diffraction [75, 76].

b) Hydrothermal crystal growth of $\text{RENiO}_3$ under high pressures

The investigated process was based on the hydrothermal crystal growth under very high pressure conditions using $\text{Nd(OH)}_3$, $\text{Ni(OH)}_2$, and $\text{KClO}_3$ (in order to maintain in situ an oxidative atmosphere) as precursors. The components were placed in a platinum capsule and treated under the following conditions: 4 GPa and 900 $^\circ$C for 15 min. Synthesis was followed by a slow cooling process 900 $^\circ$C to 600 $^\circ$C during one hour in order to improve the growth of the crystal nuclei [77, 78]. The resulting $\text{NdNiO}_3$ single crystals are presented in Fig. 13.

Differential scanning calorimetry (DSC) measurements were performed from $-140$ to 500 $^\circ$C. An endothermic peak is observed in the heating run; the reverse transition, showing an exothermic peak, is observed during the cooling run. These peaks can be assigned to the insulator $\rightarrow$ metal transition in the $\text{RENiO}_3$ perovskites (Fig. 14). The thermal hysteresis suggests that this transition is of first order for this single crystalline material.

Reactive pressure: Stabilization of the highest oxidation states of transition metals

During the last 35 years, with specific high oxygen pressure equipments (gas compression, oxidiz-
In recent years, high-pressure solutions, HP oxygen in a solid phase, have been used to stabilize unusual oxidation states of transition metals. Many unusual formal oxidation states have been stabilized in oxides (for example: Fe$^{4+}$, Fe$^{5+}$, Co$^{3+}$, Co$^{4+}$, Ni$^{3+}$, Cu$^{3+}$, Ir$^{5+}$, Ir$^{6+}$). Table 3 gives some examples of such oxides [79 – 87].

Recent reinvestigations concerned the oxide RhO$_2$. O. Muller and R. Roy prepared RhO$_2$ for the first time through oxidation of the precursor Rh$_2$O$_3$·5H$_2$O under high oxygen pressures (350 MPa, 400 – 600 °C) [88]. Recently it was confirmed that OH groups (from the thermal decomposition of Rh$_2$O$_3$·5H$_2$O (Fig. 15)) may participate in the formation of the rutile structure of RhO$_2$ according to a formulation (Rh$^{4+}$(1−x)Rh$^{3+}$xO$^{2−}$xOH$^x$) [89, 90].

In order to prevent the participation of OH groups in the RhO$_2$ structure, it was necessary to observe two conditions:

(i) a strongly oxidizing environment,
(ii) a precursor without H$_2$O or OH groups.

### Table 3. Stabilization of unusual oxidation states of transition metals of the first row under high oxygen pressures.

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation state</th>
<th>Electronic configuration</th>
<th>Oxide</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe(IV)</td>
<td>$t^3_2 !d^6 !p^5 !s^2$</td>
<td>$AE_0$(La$_1$,Sr$_1$,Ba$<em>1$.Fe$</em>{0.5}$O$_4$)</td>
<td>[79]</td>
</tr>
<tr>
<td>Fe</td>
<td>Fe(V)</td>
<td>$t^1_2 !d^6 !p^2$</td>
<td>La$_2$LiFeO$_6$</td>
<td>[80]</td>
</tr>
<tr>
<td>Co</td>
<td>Co(III)</td>
<td>LS → HS</td>
<td>$RECoO_3$ ($RE = La → Lu$)</td>
<td>[81]</td>
</tr>
<tr>
<td>Co</td>
<td>Co(IV)</td>
<td>$t^5_2 !d^5 !p^2 !s^2$</td>
<td>(Sr$<em>{0.5}$La$</em>{1.5}$Li$<em>{0.5}$Co$</em>{0.5}$O$_4$)</td>
<td>[82]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(III)</td>
<td>$t^5_2 !d^8 !p^6 !s^2$</td>
<td>$RENiO_3$ ($RE = La → Lu$)</td>
<td>[72]</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(IV)</td>
<td>$t^4_2 !d^8 !p^6 !s^2$</td>
<td>Sr$RE$NiO$_4$</td>
<td>[83]</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(III)</td>
<td>$t^6_2 !d^9 !p^6 !s^2$</td>
<td>La$_2$Li$_2$Cu$_3$O$_4$</td>
<td>[84]</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu(IV)</td>
<td>$t^3_2 !d^9 !p^6 !s^2$</td>
<td>LaCo$_3$, SrLaCu$_3$O$_4$</td>
<td>[84, 85]</td>
</tr>
<tr>
<td>Ir</td>
<td>Ir(V)</td>
<td>$t^4_2 !d^8 !p^6 !s^2$</td>
<td>La$_2$LiIrO$_6$</td>
<td>[86]</td>
</tr>
<tr>
<td>Ir</td>
<td>Ir(VI)</td>
<td>$t^3_2 !d^9 !p^6 !s^2$</td>
<td>Ba$_2$CaIrO$_6$</td>
<td>[87]</td>
</tr>
</tbody>
</table>
RhCl$_3$ was selected as the precursor and Na$_2$O$_2$ as the oxidant. Due to the limited thermal stability of Na$_2$O$_2$, its decomposition takes place before the rhodium III $\rightarrow$ IV oxidation sets in. Consequently this reaction was carried out under high oxygen pressure (200 MPa O$_2$ and 600 °C): 2 RhCl$_3$ + 3 Na$_2$O$_2$ $\rightarrow$ 2 RhO$_2$ + 6 NaCl. Sodium chloride is readily washed out with distilled water and X-ray pure rhodium dioxide can be isolated. Investigations of its physicochemical properties are in progress [91].

Conclusion

The role of high pressures in Materials Chemistry is important either for stabilizing new structural forms of materials previously prepared at ambient pressure or for preparing novel materials. On the basis of an analysis of the different effects induced by high pressure some mechanisms have been proposed for explaining structural transformations or the course of syntheses under high pressures.

The overlap of competences of six European research groups has led to the development of a network within the COST D30 programme "High pressure tuning in chemical and biochemical processes", the objective of this network being focussed on the development of materials chemistry under high pressures".

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