

Materials Chemistry under High Pressures – Some Recent Aspects

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Z. Naturforsch. **61b**, 1457 – 1470 (2006); received June 27, 2006

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) high pressures lead to the formation of novel materials from different precursors through the formation of new chemical bonds.

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) 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.

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

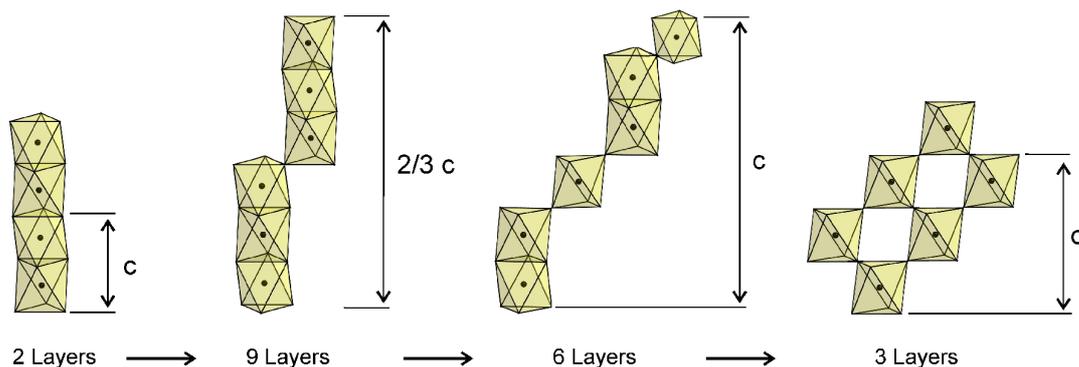


Fig. 1. Scheme for the structural evolution *vs.* pressure for some ABO_3 polytypes. Increasing pressure shifts the structure from left to right.

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

| Pressure (bar) | Medium | Energy cal/mol |
|----------------|-------------------|----------------|
| 1000 | Gas | 3000 |
| 1000 | Solid | 1 |
| 10 000 | Solid | 5 |
| 100 000 | Iron | 20 |
| 100 000 | H ₂ O | 1000 |
| 1 | Chemical reaction | 20 000 |

to the decrease of the average distances between the most highly charged cations or anions,

- (iii) the chemical-bond compressibility. If in the F_1 starting structure the compressibilities of its chemical bonds are different, this structure can be changed under high pressures.

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 ΔV 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 ΔV 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 (qq'/d^2), thus causing instability. In order to reduce these adverse effects, the structure is changed 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

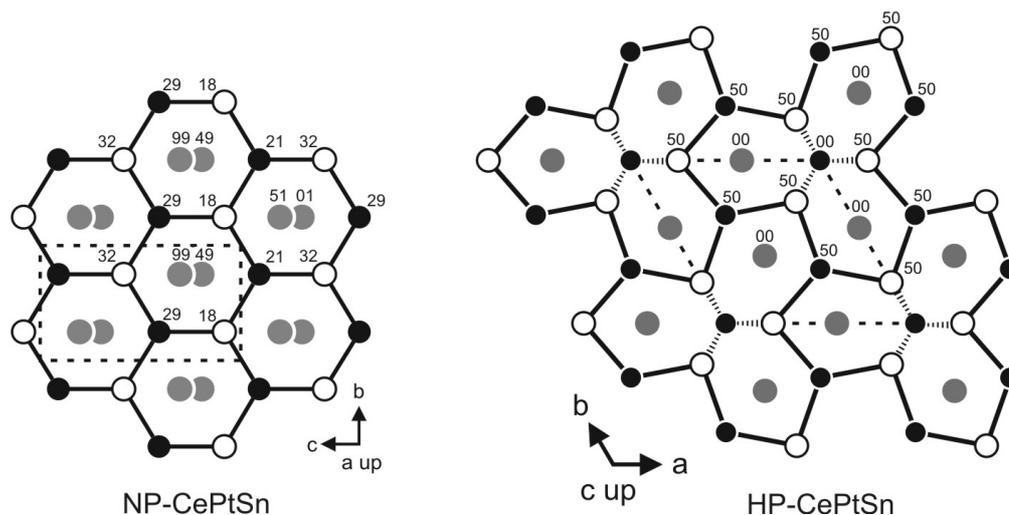


Fig. 2. Projection of the crystal structures of the normal and high-pressure modifications of the stannide CePtSn.

involved. Considering that the cation coordination is correlated to the cation-anion distance (C–A), modification of such cation-anion distances for different cations C_1, C_2, \dots 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 ΔV value:

$$\begin{aligned} [V/Z(\text{HP-CePtSn}) - V/Z(\text{NP-CePtSn})] \\ = 68.7 \text{ \AA}^3 - 69.3 \text{ \AA}^3 = -0.6 \text{ \AA}^3, \end{aligned}$$

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.* $d(\text{Ce-Ce})$ NP-CePtSn $\sim 4.12 \text{ \AA}$ and $d(\text{Ce-Ce})$ HP-CePtSn \sim

4.02 \AA . Thus we observe a significant reduction during this high-pressure structure transformation. Due to the electronic structure of the rare earth elements (filling of $4f$ 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.

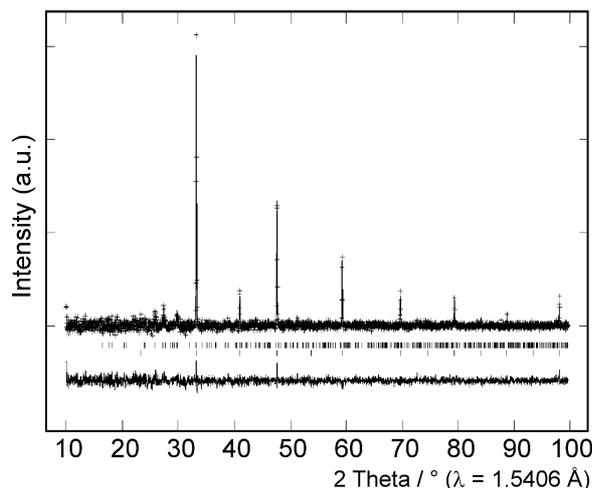


Fig. 3. X-ray diffraction pattern of SrCrO₃.

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 ΔV 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: MnO₂,

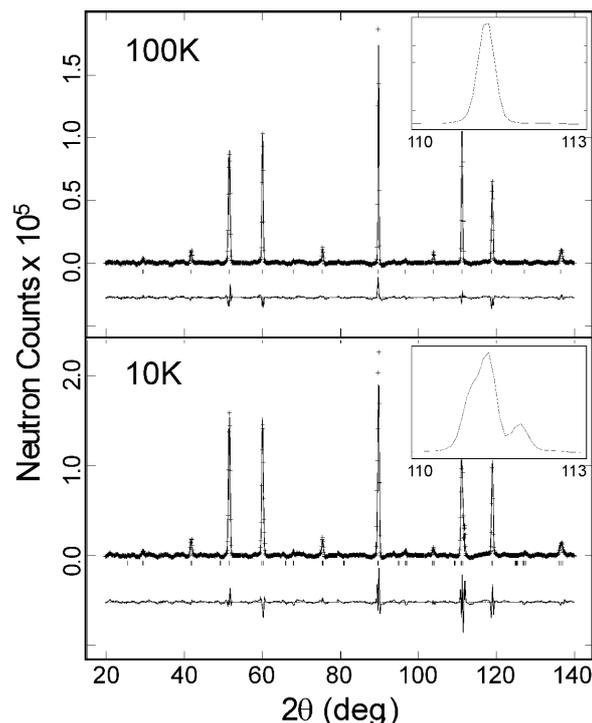


Fig. 4. Neutron diffraction patterns of SrCrO₃ at 10 and 100 K (according to [18]).

HgO, PbO₂, ...) is increased beyond the reaction temperature [15, 16].

Synthesis of the SrCrO₃ 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, SrCrO₃ was revisited, with high pressures applied for stabilizing the CrO₂ used as a precursor [18]. Cr(IV) is not stable owing to two decomposition pathways:

- (i) thermal deoxygenation:
 $2 \text{CrO}_2 \rightarrow \text{Cr}_2\text{O}_3 + 1/2 \text{O}_2$ and
- (ii) Cr(IV) disproportionation:
 $3 \text{Cr(IV)} (\text{O}_h) \rightarrow 2 \text{Cr(III)} (\text{O}_h) + 1 \text{Cr(VI)} (T_d)$.

Fig. 3 shows the X-ray diffraction pattern of SrCrO₃ 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-

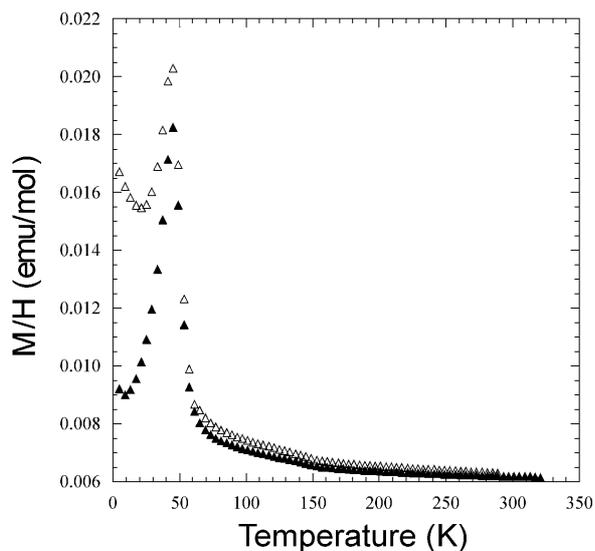


Fig. 5. Zero-field and field cooled magnetic susceptibility data for SrCrO_3 (from [18]).

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_3N_5

Recently, it was possible to stabilize new forms of nitrides using high pressures. The thermal stabilization of P_3N_5 has led to investigations of its structural transformations, and a new high-pressure phase, $\gamma\text{-P}_3\text{N}_5$, was stabilized [19]. The normal-pressure and high-pressure forms are shown in Fig. 6. In contrast to the

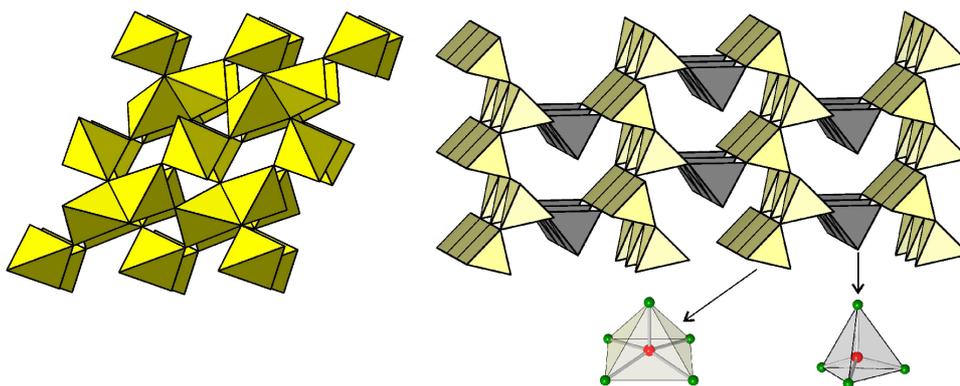


Fig. 6. Schematic views of both the normal-pressure $\alpha\text{-P}_3\text{N}_5$ (left) and the high-pressure $\gamma\text{-P}_3\text{N}_5$ (right) structures.

normal-pressure modification $\alpha\text{-P}_3\text{N}_5$ [20], which is built up from corner- and edge-sharing PN_4 tetrahedra, the structure of the high-pressure modification $\gamma\text{-P}_3\text{N}_5$ 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_3N_4 phase under high pressures. The normal-pressure α - and $\beta\text{-Si}_3\text{N}_4$ modifications contain exclusively (SiN_4) units, while the high pressure $\gamma\text{-Si}_3\text{N}_4$ 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 $\text{RE}_2\text{O}_3\text{-B}_2\text{O}_3$

The chemical system $\text{RE}_2\text{O}_3\text{-B}_2\text{O}_3$ was recently investigated under high-pressure conditions [23]. At normal pressure, three different compositions are observed: REBO_3 , RE_3BO_6 , and REB_3O_6 [24]. Under high pressures, three new compositions of rare earth borates have been prepared depending on the size of the metal: $\alpha\text{-RE}_2\text{B}_4\text{O}_9$ (with $\text{RE} = \text{Eu, Gd, Tb, Dy}$) [25], $\text{RE}_4\text{B}_6\text{O}_{15}$ (with $\text{RE} = \text{Dy, Ho}$) [26], and $\text{RE}_3\text{B}_5\text{O}_{12}$ (for $\text{RE} = \text{Er-Lu}$) [27]. If we compare the $\Delta V/Z$ of the precursors to the V/Z of the HP phases, in all cases the ΔV 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

Table 2. Evaluation of the ΔV values for selected high-pressure phases in the system RE_2O_3 – B_2O_3 .

| α - $RE_2B_4O_9$: | | | |
|---------------------------|--------------|-------|------------|
| RE | $\Sigma V/Z$ | V/Z | ΔV |
| Eu | 170.6 | 139.1 | -31.5 |
| Gd | 169.0 | 138.1 | -30.1 |
| Dy | 166.5 | 135.5 | -31.0 |
| Ho | 164.4 | 134.4 | -30.0 |
| $RE_4B_6O_{15}$: | | | |
| RE | $\Sigma V/Z$ | V/Z | ΔV |
| Dy | 287.7 | 240.0 | -47.7 |
| Ho | 283.8 | 238.3 | -45.5 |
| $RE_3B_5O_{12}$: | | | |
| RE | $\Sigma V/Z$ | V/Z | ΔV |
| Er | 222.8 | 186.3 | -36.5 |
| Tm | 220.7 | 183.9 | -36.8 |
| Yb | 221.0 | 182.6 | -38.4 |
| Lu | 219.2 | 181.0 | -38.2 |

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 $AA'_3B_4O_{12}$ [31],
- (iii) Synthesis of perovskites $Sr_3Cr_2ReO_9$ and $SrCr_xRu_{1-x}O_3$ [18, 32].

Synthesis of the perovskites $SeMO_3$ with $M^{2+} = Mn, Co, Ni, Cu, and Zn$

The precursors were H_2SeO_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 $124-130^\circ$. Such an effect was also observed for a Bi^{3+} perovskite ($BiNiO_3$ for which a

$(Bi_{0.50}^{3+}Bi_{0.50}^{5+})Ni^{2+}O_3$ oxidation state distribution has been proposed [33, 34]). In fact, Se^{4+} as a $4s^2$ cation is too small ($\sim 0.50 \text{ \AA}$) 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].

Synthesis of the *pseudo*-perovskites $AA'_3B_4O_{12}$

The *pseudo*-perovskite $CaCu_3Mn_4O_{12}$ 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 $RECu_3Mn_4O_{12}$ (RE from La^{3+} to Yb^{3+}) have thus been prepared under moderate pressure conditions ($p = 2 \text{ GPa}$ and $T = 1000 \text{ }^\circ\text{C}$) 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 $RECu_3Mn_4O_{12}$ 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 $3d$ (Mn) and $2p$ (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].

$AA'_3B_4O_{12}$ - $CaCu_3Mn_4O_{12}$

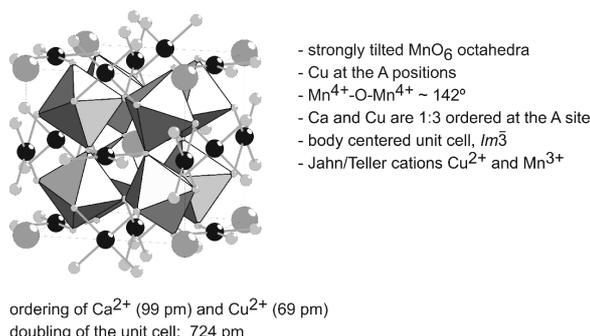


Fig. 7. Structure of the *pseudo*-perovskites with the general formula $AA'_3B_4O_{12}$.

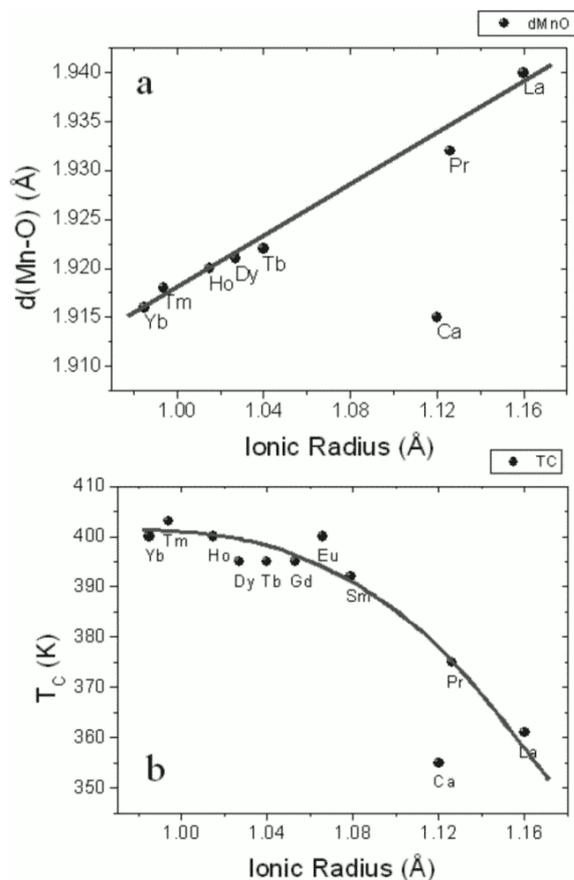


Fig. 8. Evolution of the $d(\text{Mn-O})$ distance in the $\text{RECu}_3\text{Mn}_4\text{O}_{12}$ structures vs. the RE^{3+} ionic radius (8a) and the influence on the T_C value (8b).

High-pressure synthesis of double perovskites

High pressures are required in many cases for stabilizing double perovskites $\text{A}_2\text{BB}'\text{O}_6$ [40]. In these cases, different effects can support the synthesis: (i) the “densification effect” favouring the coordination number VI, (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 $\text{Sr}_3\text{Cr}_2\text{ReO}_9$ [$\text{Sr}(\text{Cr}_{2/3}\text{Re}_{1/3})\text{O}_3$]

The selected precursors were SrO , Cr_2O_3 , and ReO_3 . Under normal pressure conditions this compound is not obtained and the formation of Cr^{6+} is observed. In order to prevent the formation of Cr^{6+} through the destabilization of its tetrahedral coordination, high pressures have been used for preparing

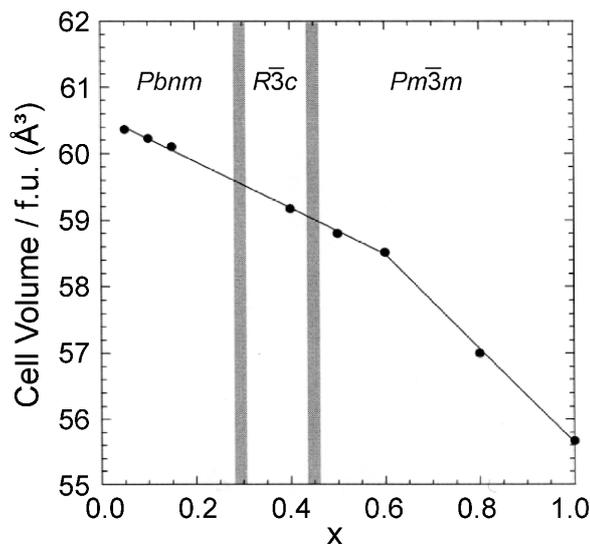


Fig. 9. Structural evolution in the system $\text{SrCr}_x\text{Ru}_{1-x}\text{O}_3$ (according to [18]).

$\text{Sr}_3\text{Cr}_2\text{ReO}_9$ [32], with Cr^{3+} and Re^{6+} being stabilized in octahedral coordination. This new perovskite shows a ferrimagnetic ordering below $T_C = 130$ K.

(ii) Preparation of solid solutions of SrCrO_3 and 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 favour 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

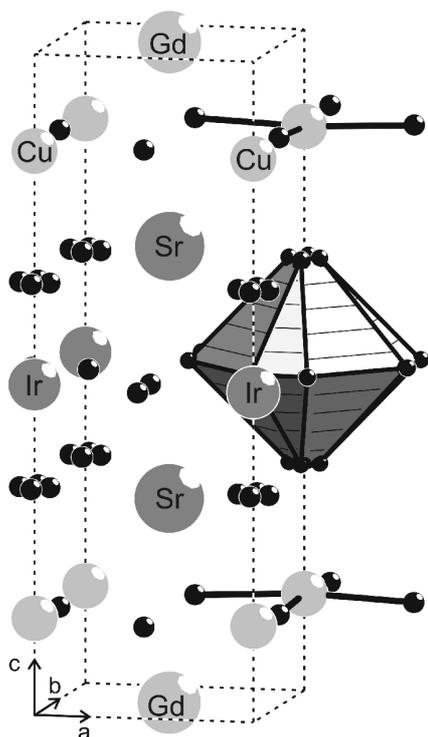


Fig. 10. The crystal structure of $\text{IrSr}_2\text{GdCu}_2\text{O}_8$. The octahedral IrO_6 and square planar CuO_4 environments are emphasized. Note that the oxygen atoms around iridium were refined with split positions. For details see [53].

case of the $\text{RE}_2\text{M}_2\text{O}_7$ pyrochlore structure, the limit of stability is defined by $r_A/r_M \approx 1.55$, in spite of the r_A/r_M ratio being close to 1.8 under normal conditions. Due to the difference of the compressibility between rare earth RE^{3+} and Ge^{4+} it was possible to prepare the $\text{RE}_2\text{Ge}^{4+}\text{O}_7$ series (RE = rare earth) with the pyrochlore structure under high-pressure conditions [41].

Another example is the preparation of the RE_2CuO_4 oxides. The Nd_2CuO_4 -type structure can be stabilized through the synthesis at ambient pressure for RE cations from Nd to Gd [42–44]. From simple geometrical considerations, the cubic eight-fold coordination of oxygen for RE^{3+} is stabilized for $r_{\text{RE}}/r_{\text{O}} > 0.73$. Consequently, compounds RE_2CuO_4 with $r_{\text{RE}}/r_{\text{O}} < 0.73$ cannot be obtained at ambient pressure. Using high-pressure conditions (6 GPa), the RE_2CuO_4 (RE = Y, Dy, Ho, Er, Tm) materials with the Nd_2CuO_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].

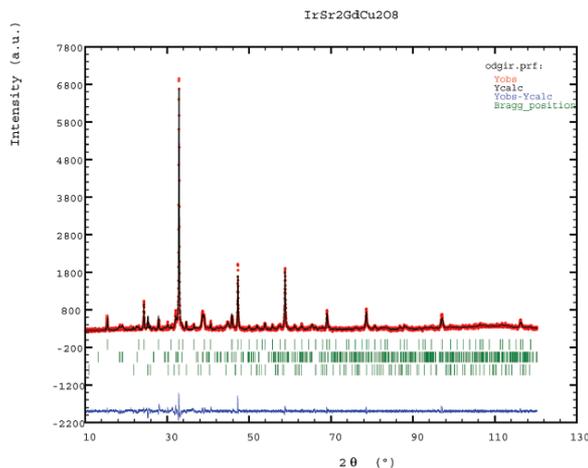


Fig. 11. Rietveld refinement plot of the X-ray diffraction data for (1) $\text{IrSr}_2\text{GdCu}_2\text{O}_8$ and the two impurity phases (2) $\text{Sr}_3\text{IrCuO}_6$ and (3) SrCuO_2 (Figure taken from [53]).

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 s^1d^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 s^0d^1 and potassium acquires chemical properties comparable to a transition metal. This phenomenon can explain the formation of intermetallic compounds (K_xAg_y) under very high pressures using diamond anvil cells [48, 49].

Another recent example is the high-pressure synthesis of novel metalocuprates $\text{TSr}_2\text{RECu}_2\text{O}_8$ (T = Cr, Ir, ...). The interest in these materials arose when superconductivity (at ~ 30 K) and magnetic ordering (at ~ 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 Cr^{4+} in octahedral coordination [52]. Iridium also may enter the structure giving rise to a novel ferrimagnetic material. The structure is shown in

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 $RE = \text{gadolinium}$.

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 $4f$ orbitals ($\text{Gd } 4f^7$).

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 kinetics of the chemical reactions

The development of Materials Chemistry under high pressures using solid precursors has demonstrated the strong effect of the kinetics on materials preparations. For example, from La_2O_3 and Fe_2O_3 as solid precursors, the synthesis of the perovskite LaFeO_3 requires at normal pressure and 1000°C about 70 h. Using a pressure close to 5 GPa and the same temperature (1000°C), only 10 min are necessary to obtain a pure perovskite phase [6]. The induction effects are not well understood and it will be important to improve pertinent knowledge. In other cases, due to the low reactivity of some precursors (such as CdO), high pressures can help in the synthesis of new perovskites such as CdVO_3 [54].

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 - α , 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 ($RE = \text{Y, La} \rightarrow \text{Lu}$) and TiNiO_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 $\text{Ni}^{3+}\text{O} - \text{Ni}^{3+}$ angle is reduced from 165° for LaNiO_3 to 145° for LuNiO_3 , inducing a decrease of the overlap between $3d(\text{Ni}^{3+})$ and $2p(\text{O}^{2-})$ orbitals. A metal \rightarrow insulator transition is observed following the decrease of the RE^{3+} cation size ($\text{La} \rightarrow \text{Lu}$) [72]. For the same RE^{3+} cation an insulator \rightarrow metal transition is also observed *versus* T due to the gradual opening of the $\text{Ni}-\text{O}-\text{Ni}$ 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,

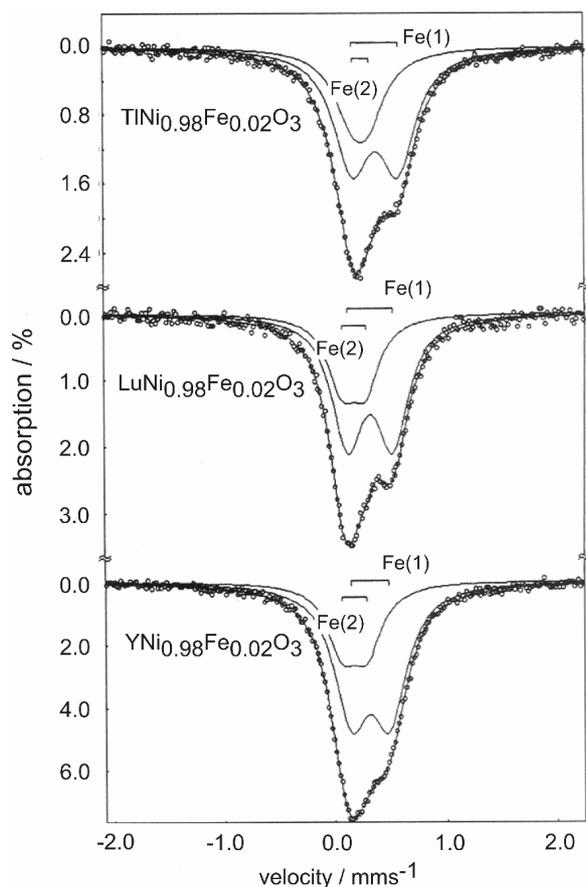


Fig. 12. ^{57}Fe Mössbauer spectra of $\text{ANi}_{0.98}\text{Fe}_{0.02}\text{O}_3$ ($A = \text{Ti, Lu, Y}$) at 300 K. For details see [75].

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

The RENiO_3 perovskites were investigated in order

- to detect the specific electronic phenomena (in particular disproportionation) using a local probe (^{57}Fe Mössbauer spectroscopy),
- 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 Ni^{3+} disproportionation in the RENiO_3 perovskites

Recently, using ^{57}Fe Mössbauer spectroscopy on ^{57}Fe doped RENiO_3 nickelates, two different posi-

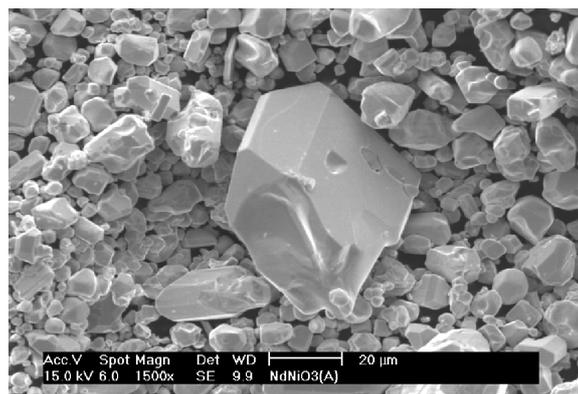


Fig. 13. Single crystal of NdNiO_3 prepared through a hydrothermal process.

tions have been assigned for ^{57}Fe (Fig. 12). This result was taken as evidence for two types of nickel positions in the RENiO_3 structure corresponding to two different nickel species: $\text{Ni}^{(3+\sigma)+}$ and $\text{Ni}^{(3-\sigma)+}$, and confirming the results obtained through neutron diffraction [75, 76].

b) Hydrothermal crystal growth of RENiO_3 under high pressures

The investigated process was based on the hydrothermal crystal growth under very high pressure conditions using $\text{Nd}(\text{OH})_3$, $\text{Ni}(\text{OH})_2$, and 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 °C for 15 min. Synthesis was followed by a slow cooling process 900 °C \rightarrow 600 °C during one hour in order to improve the growth of the crystal nuclei [77, 78]. The resulting NdNiO_3 single crystals are presented in Fig. 13.

Differential scanning calorimetry (DSC) measurements were performed from -140 to 500 °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 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-

| Element | Oxidation state | Electronic configuration | Oxide | Ref. |
|---------|-----------------|--|--|------------------|
| Fe | Fe(IV) | $t_{2g}^3 d_{z^2}^1 d_{x^2-y^2}^0$ | $AE_{0.5}La_{1.5}Li_{0.5}Fe_{0.5}O_4$ $AE = Ca, Sr, Ba$ | [79] |
| Fe | Fe(V) | $t_{2g}^3 e_g^0$ | La_2LiFeO_6 | [80] |
| Co | Co(III) | LS \rightarrow HS | $RECoO_3$ ($RE = La \rightarrow Lu$) | [81] |
| Co | Co(IV) | $t_{2g}^6 e_g^0$ | $(Sr_{0.5}La_{1.5})Li_{0.5}Co_{0.5}O_4$ | [82] |
| Ni | Ni(III) | $t_{2g}^6 \sigma^{*1}$ | $RENiO_3$ ($RE = La \rightarrow Lu$) $SrRENiO_4$ | [72] [83] |
| Cu | Cu(III) | $t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0$ $t_{2g}^6 \sigma^{*2}$ | $La_2Li_{0.5}Cu_{0.5}O_4$ $LaCuO_3, SrLaCuO_4$ | [84] [84, 85] |
| Ir | Ir(V) | $t_{2g}^4 e_g^0$ | La_2LiIrO_6 | [86] |
| Ir | Ir(VI) | $t_{2g}^3 e_g^0$ | Ba_2CaIrO_6 | [87] |

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

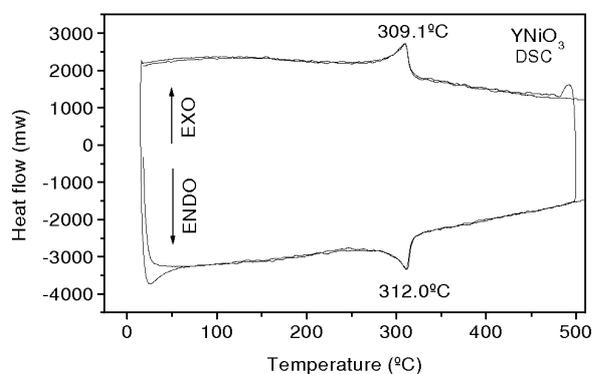
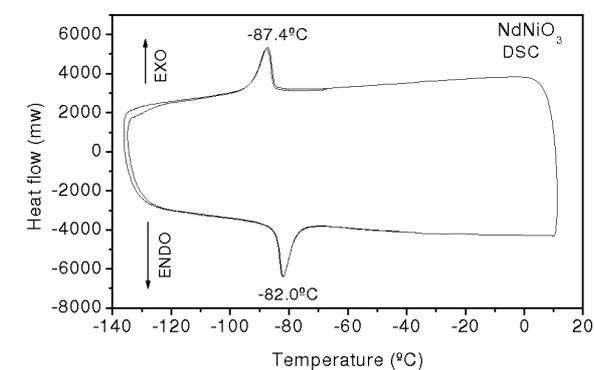


Fig. 14. Differential scanning calorimetry measurements on $NdNiO_3$ and $YNiO_3$ single crystals versus temperature ($143 < T < 773$ K). For details see [77].

ing solutions, HP oxygen in a solid phase) many unusual formal oxidation states were 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].

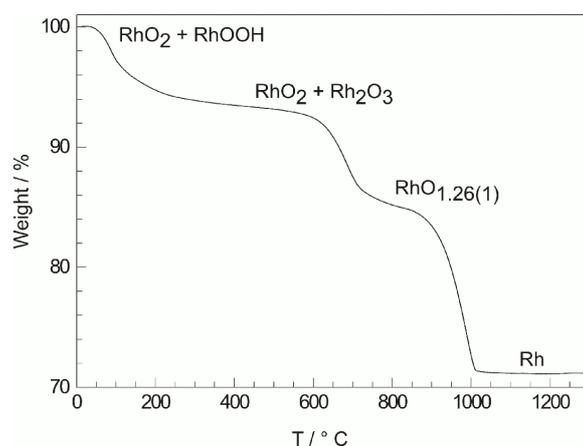


Fig. 15. Thermogravimetric analysis of the “ RhO_2 ” sample prepared under high oxygen pressure from $Rh_2O_3 \cdot 5H_2O$ as precursor [91]. Thermogravimetry was performed in flowing N_2 (ca. 50 mL/h) in the temperature range 20–1300 °C using a SETARAM TAG24 setup. 17.02 mg of the sample was placed in a corundum sample holder and the temperature was raised with 10 °/min.

Recent reinvestigations concerned the oxide RhO_2 . O. Muller and R. Roy prepared RhO_2 for the first time through oxidation of the precursor $Rh_2O_3 \cdot 5H_2O$ under high oxygen pressures (350 MPa, 400–600 °C) [88]. Recently it was confirmed that OH groups (from the thermal decomposition of $Rh_2O_3 \cdot 5H_2O$ (Fig. 15)) may participate in the formation of the rutile structure of RhO_2 according to a formulation $(Rh^{4+}_{(1-x)}Rh^{3+}_xO_{(2-x)}OH_x)$ [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_2O or OH groups.

RhCl₃ was selected as the precursor and Na₂O₂ as the oxidant. Due to the limited thermal stability of Na₂O₂, its decomposition takes place before the rhodium III → IV oxidation sets in. Consequently this reaction was carried out under high oxygen pressure (200 MPa O₂ and 600 °C): 2 RhCl₃ + 3 Na₂O₂ → 2 RhO₂ + 6 NaCl. Sodium chloride is readily washed out with distilled water and X-ray pure rhodium dioxide can be isolated. Investigations of its physico-chemical 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 anal-

ysis 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".

Acknowledgements

The authors thank the COST-ESF programme D-30 for support for the organization of Working Group Meetings and short term scientific missions for young researchers. Part of this work was also funded by the Deutsche Forschungsgemeinschaft (DFG; PO 573/10-1, HU 966/4-1, and HU 966/2-2).

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