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High pressures and chemical reactivity: an approach to the synthesis of novel materials

G rard Demazeau*

CNRS, Universit  de Bordeaux, ICMCB – Site de l'ENSCP, Pessac, France

In material synthesis, high pressures are characterized by different factors: the weak conveyed energy compared to the temperature; the negative ΔV value (if ΔV is the volume difference between the final unit-cell volume of the resulting material and the sum of the unit-cell volumes of the precursors); the 'in situ' improvement of the chemical reactivity inducing rapid reaction kinetics (such an improvement being observed in particular in the presence of a liquid phase as solvothermal processes). In addition, the reaction mechanisms and the chemical reactivity of the precursors can play an important role in high-pressure synthesis. Consequently, in order to develop new high-pressure research domains involving novel materials, careful selection of either the reaction route or the chemical nature of precursors appears as a fruitful approach for decreasing the pressure and temperature conditions required for the synthesis. In particular, such an approach is important for the synthesis of novel materials characterized by specific physical properties (hardness, magnetic or electrical properties, etc.) able to lead to industrial developments.

Keywords: high pressures; reaction mechanisms; chemical nature of precursors; experimental conditions

1. Introduction

Material synthesis, through processes involving different precursors as solid phases, very often requires high temperatures in order to activate the chemical diffusion of reactive species. Such a requirement can be considered as a negative factor, in particular, in two cases:

- the preparation of low-temperature structural forms;
- the stabilization of metastable materials.

Different strategies have been set-up in order to bypass the use of high temperatures: in particular, the development of high pressures and the selection of either appropriate reaction mechanisms or the chemical nature of precursors.

This paper presents an analysis of each strategy and some illustrative examples.

*Email: demazeau@icmcb-bordeaux.cnrs.fr

2. Synthesis of novel materials under high pressures

The application of high pressures is characterized by three main factors:

- the small energy developed by pressure in liquid or solid phases (such energy being directly correlated to the compressibility of the medium submitted to pressure);
- the negative ΔV value, if ΔV is defined as

$$\Delta V = \sum \left(\frac{V_j}{Z_j} \text{ final materials} \right) - \left(\frac{V_i}{Z_i} \text{ precursors} \right),$$

where V/Z corresponds to the volume per unit formula with (j) for the products and (i) for the reagents;

- the improvement of the chemical reactivity.

The energy conveyed by high pressures in solid-state synthesis or in reaction processes involving a liquid phase (as solvothermal processes) is small, and such a parameter can be negligible compared to temperature effects.

The chemical reactivity seems to be improved due to the observed kinetic effects during solid-state synthesis (e.g., using Fe_2O_3 and La_2O_3 as precursors at a constant temperature (1000°C), 70 h is required for obtaining a pure perovskite-phase LaFeO_3 at normal pressure (10^5 Pa) and only 5 min using high pressures close to 5 GPa [1]). High pressures – in a first analysis – could appear as an expansive technique, but due to the low energy conveyed by the pressure parameter, the running cost is small compared to the conventional ceramic processes. The investment is important but the certified number of runs is now improved.

During these last 50 years, high pressures have been developed for preparing different new materials [2–4]. The relevant question could be, in the near future: how to combine pressure as a thermodynamic variable with the chemical reactivity for improving the domains of materials synthesis?

Two main strategies have been developed for associating high pressures and chemical reactivity:

- the development of specific media or chemical processes under high pressures;
- the selection of the chemical nature of precursors through low-temperature preparation processes or specific pretreatments (as mechanical milling).

3. Material synthesis using specific reactive media or chemical processes under high-pressure conditions

During the last 30 years, solvothermal reactions were developed, the use of specific solvents (aqueous or non-aqueous) improving the chemical reactivity either in a homogeneous system or a heterogeneous one in sub- or supercritical conditions [5].

Solvothermal reactions are characterized by a chemical reaction between precursors in a close system in the presence of a specific solvent and at a temperature higher than the boiling temperature of that solvent. Consequently, pressure is involved as autogenous pressure (if the pressure value is regulated both by the percentage of filling for the high-pressure vessel and the selected temperature) or as imposed pressure using at the beginning of the solvent under high pressure.

Solvothermal reactions can help the synthesis of novel materials with a specific structure (as the phyllosiloxides isostructural of the natural phyllosilicates), or can orientate the formation of metastable materials if the synthesis is kinetically controlled (as the stabilization of the metastable structural forms of MnS versus the physico-chemical properties of the solvent).

3.1. Solvothermal synthesis of the phyllosiloxides

The origin of this research was to find layered materials able to be developed as interphases between fiber and matrix in order to deflect cracks from mode 1 (perpendicular to the fiber) to mode 2 (parallel to the fiber) and able to be used at high temperature ($T > 1000^\circ\text{C}$) in an oxygen atmosphere [6]. Graphite and hexagonal BN, being oxygen sensitive in such a temperature range, and the thermal stability of phyllosilicates (as mica) being reduced due to the presence of hydroxyl groups [$2\text{OH}^- \rightarrow \text{H}_2\text{O} (\text{vapor}) + \text{O}^{2-}$] leading to the formation of anionic vacancies, a new family of layered oxides derived from natural phyllosilicates was prepared.

Using mica with the phlogopite structure as a structural model, a new composition was set-up through different substitutions: anionic ($\text{OH}^- \rightarrow \text{O}^{2-}$) and cationic ($\text{Al}^{3+} \rightarrow \text{Si}^{4+}$ in T_d sites and $\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$ in O_h sites) (Figure 1).

In order to synthesize such a proposed complex composition, a homogeneous precursor has been prepared through a sol-gel process. In a second step, this precursor (aerogel) has been treated using a conventional solid-state chemistry process ($500^\circ\text{C} < T < 1000^\circ\text{C}$). X-ray diffraction patterns of the resulting materials confirm that only a mixture of 3D silicates is formed.

Through a solvothermal process, using as solvent the same as that for preparing the sol (2-methoxy-ethanol) and the following experimental conditions ($50 < P < 150 \text{ MPa}$, $T = 600^\circ\text{C}$, $t = 54 \text{ h}$), a single-phase isostructural of mica with the phlogopite structure is observed through X-ray diffraction analysis. The physical characterizations (IR spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM)) confirm both the absence of hydroxyl group into the lattice and the lamellar structure of this material (Figure 2).

Consequently, using a solvothermal process, a new family of 2D oxides, isostructural of natural phyllosilicates, has been prepared for the first time [7,8].

3.2. Stabilization of metastable materials

The stabilization of metastable materials is important for enlarging the knowledge in material chemistry [9]. When the synthesis is kinetically controlled, metastable materials can be stabilized.

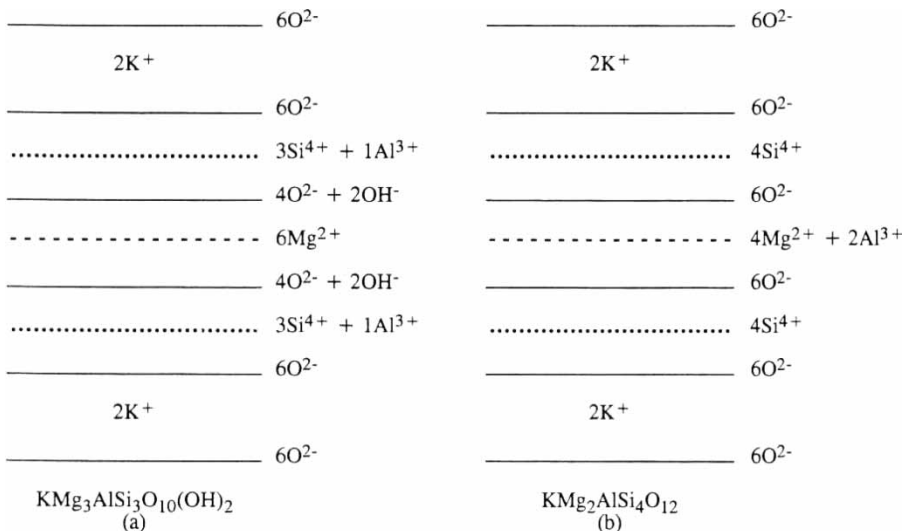


Figure 1. Proposal for a new layered oxide, isostructural of mica with the phlogopite structure ($\text{KMg}_3(\text{AlSi}_3)\text{O}_{10}(\text{OH})_2$), through the anionic substitution ($\text{OH}^- \rightarrow \text{O}^{2-}$) compensated by cationic substitutions either on the T_d sites ($\text{Al}^{3+} \rightarrow \text{Si}^{4+}$) or O_h sites ($\text{Mg}^{2+} \rightarrow \text{Al}^{3+}$).

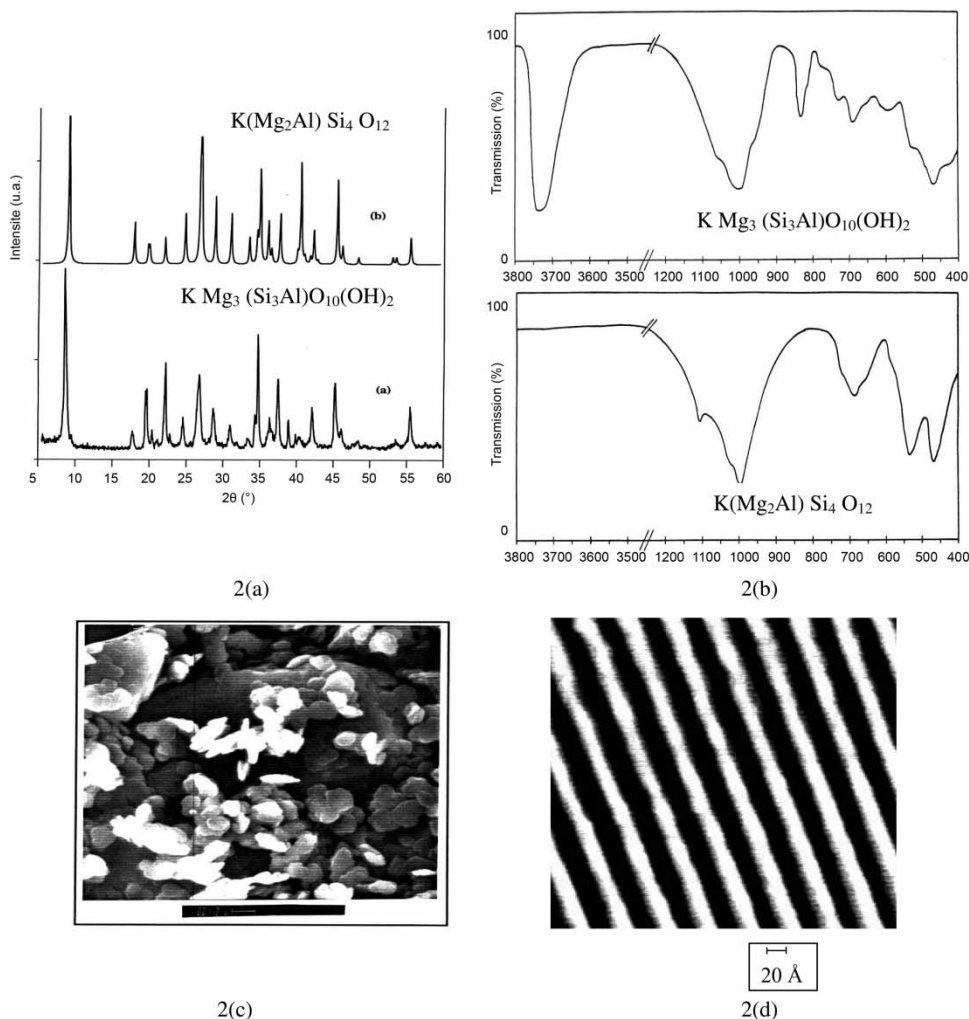


Figure 2. Physico-chemical characterizations of the single phase issued from solvothermal synthesis: (a) comparison of the X-ray diffraction patterns; (b) comparison of the IR spectra; (c) SEM of the single phase and (d) TES.

Using $MnCl_2$, $4H_2O$ and $SC(NH_2)_2$ as precursors, the solvothermal preparation of MnS with the stable α -rocksalt form or the metastable β and γ forms (zinc-blende and wurtzite structures) is closely dependent on the chemical nature of the solvent.

When the solvent (water or ethylenediamine) is able to form a stable Mn^{2+} complex, the stable α -rocksalt structure is observed. When the solvent is THF or benzene, the β zinc-blende structure and the γ -wurtzite structure were, respectively, stabilized [10].

Such an example underlines the role of the chemical mechanisms governing the solvothermal preparation process on the stabilization of metastable or stable structural forms for the same chemical composition.

The decomposition temperature of $SC(NH_2)_2$ ($180^{\circ}C$) as S^{2-} source being relatively high, a solvothermal reaction in lower temperature conditions (60 – $130^{\circ}C$) using different precursors (thioacetamide and $Mn(CH_3COO)_2$) and water as solvent has led to the formation of the γ -MnS form [11]. Such a result would underline that the temperature would be a predominant parameter, compared to the nature of the solvent (ability to form a complex with Mn^{2+}), on the stabilization of a metastable structural form for MnS.

4. Material synthesis through chemical reactive precursors

High pressures due to the small energy involved in material chemistry are, in different cases, not sufficient for inducing the synthesis. Consequently, the improvement of the chemical reactivity for the precursors appears to be a possible strategy for improving material synthesis under high-pressure conditions. For illustrating such a strategy, several methods have been developed involving, in particular, either the preparation method of the precursor(s) or different characteristics of the reagent(s) (texturation, structure, etc.).

4.1. *Synthesis of different compounds using precursors obtained by wet chemistry techniques*

The perovskites with A cationic ordering ($A'A_3$)B₄O₁₂ exhibit interesting physical properties (magnetism, low-field magnetoresistance, etc.) [12]. CaCu₃Mn₄O₁₂ and other compounds of the ($A'A_3$)B₄O₁₂ family require, using oxides as precursors, in the main cases, high pressures (close to 5 GPa) for obtaining a pure phase [13]. Recently, new derivatives of CaCu₃Mn₄O₁₂ were prepared at a lower pressure (2 GPa) in the same temperature domain ($\approx 1000^\circ\text{C}$) using very reactive precursors obtained by wet chemistry procedures (Ca^{2+} being replaced by rare earth) [14].

4.2. *Synthesis of diamond versus the structure of the graphite source*

The reactivity of transition metals with carbon plays an important role on the flux-assisted conversion graphite \rightarrow diamond. The ability for a transition metal to react with carbon increases with its number of electron vacancies in the d-orbitals [15]. The mechanisms of diamond formation proceed in two steps: nucleation and growth. Graphite structures may determine the rate of diamond nucleation [16]. In addition, the structural relationship between diamond and graphite may also include the inheritance of texture [15]. Consequently, the high-pressure synthesis of diamond requires controlling the preparation of the graphite precursor.

4.3. *Synthesis of LaCuO₃ using a precursor characterized by a specific structure*

The stabilization of Cu^{3+} in oxygen lattices was obtained at the beginning of the 1970s [17,18]. For preparing under very high oxygen pressures, LaCuO₃ with the perovskite structure and metallic behavior, La₂CuO₄ and CuO were used as precursors [17]. Recently, in order to investigate electronic properties of Cu^{3+} in such a LaCuO₃ lattice through Mössbauer spectroscopy, it was necessary to dope LaCuO₃ lattice with 1% ^{57}Fe .

With La₂CuO₄ and CuO [doped with ^{57}Fe (1%)] as precursors, and the same experimental conditions that were used for the undoped material (6 GPa, 950°C in the presence of KClO₃ as an oxygen source) no pure Cu^{3+} perovskite was observed.

The preparation of the ^{57}Fe -doped LaCuO₃ required two steps: (i) the reaction between the precursors and (ii) the copper oxidation ($\text{Cu}^{2+} \rightarrow \text{Cu}^{3+}$). A new precursor, La₂Cu₂O₅, was selected in order to reduce the preparation process to the second step. La₂Cu₂O₅ can adopt two different structural forms: orthorhombic [19] and monoclinic [20]. LaCu₂O₅ (doped with ^{57}Fe (2%)) was prepared with the two structural forms. Using oxygen pressures in a Walker-type module apparatus (using KClO₃ as oxygen source), only the orthorhombic form is transformed to pure LaCuO₃: 1% ^{57}Fe (11.5 GPa, 900°C) [21]. Such a result can be explained through the specific structure of the orthorhombic form La₂Cu₂O₅ isomorphous with Ca₂Mn₂O₅. Cu^{2+} occupying a (CuO₅) square pyramid in such a structure. The transformation ($\text{La}_2\text{Cu}_2\text{O}_5$: $^{57}\text{Fe} \rightarrow 2 \text{LaCuO}_3$: ^{57}Fe)

is associated with a high-pressure diffusion of oxygen into the bulk of the orthorhombic matrix $[(\text{CuO}_5) + \frac{1}{2}\text{O}_2 \rightarrow (\text{CuO}_6)]$.

Using $\text{La}_2\text{Cu}_2\text{O}_5$: ^{57}Fe with a monoclinic structure, characterized by two different Cu^{2+} environments (square planar and octahedral) and with the same experimental P , T conditions, no pure perovskite phase was observed.

Consequently, the structure of the precursor, and in particular the repartition of oxygen vacancies, can play an important role for preparing the target material under high pressures.

5. Conclusions

High pressure is an important tool for preparing new materials. Two factors play a crucial role: (1) the negative ΔV value, and (2) the increase of the chemical reactivity. Nevertheless, in order to enlarge the application domain of high pressures, chemical reactivity must be improved through (i) the development of specific media or chemical processes under high pressures and/or (ii) the selection of the chemical nature (in particular, the preparation method) or the structural form of the precursors.

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