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► **To cite this version:**

G rard Demazeau. High pressures and chemical reactivity: an approach to the synthesis of novel materials. High Pressure Research, 2008, PROCEEDINGS OF THE XLVI TH EUROPEAN HIGH PRESSURE RESEARCH GROUP (EHPRG 46) MEETING, VALENCIA (SPAIN), 7–12 SEPTEMBER 2008, 28 (4), pp.483-489. 10.1080/08957950802492134 . hal-00348841

**HAL Id: hal-00348841**

**<https://hal.science/hal-00348841>**

Submitted on 13 May 2022

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

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In material synthesis, high pressures are characterized by different factors: the weak conveyed energy compared to the temperature; the negative  $\Delta V$  value (if  $\Delta V$  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.

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## 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  $\Delta V$  value, if  $\Delta V$  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  $\text{Fe}_2\text{O}_3$  and  $\text{La}_2\text{O}_3$  as precursors at a constant temperature ( $1000^\circ\text{C}$ ), 70 h is required for obtaining a pure perovskite-phase  $\text{LaFeO}_3$  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  $\text{MnS}$  versus the physico-chemical properties of the solvent).



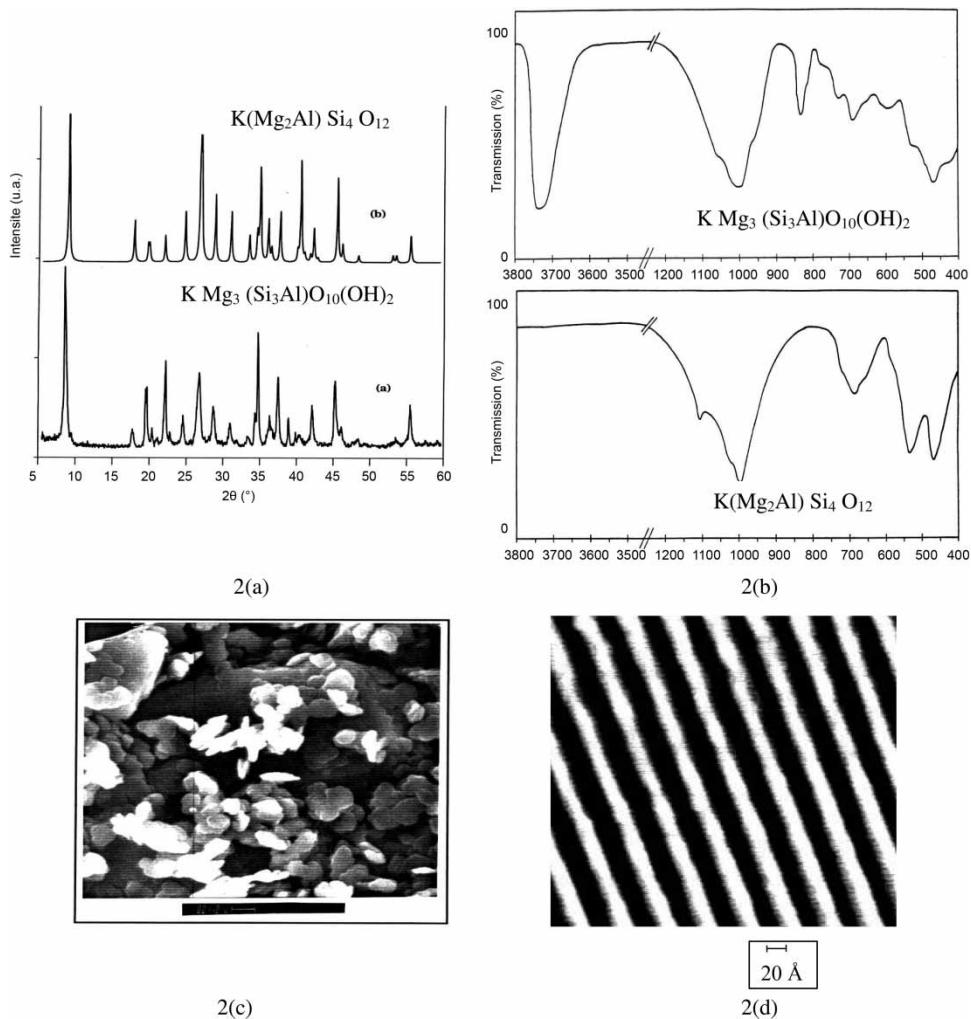


Figure 2. Physico-chemical characterizations of the single phase issued from solvothermal synthesis: (a) comparison of the X-ray diffraction patterns; (b) comparison of the IR spectra; (c) SEM of the single phase and (d) TES.

Using  $MnCl_2$ ,  $4H_2O$  and  $SC(NH_2)_2$  as precursors, the solvothermal preparation of MnS with the stable  $\alpha$ -rocksalt form or the metastable  $\beta$  and  $\gamma$  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  $\alpha$ -rocksalt structure is observed. When the solvent is THF or benzene, the  $\beta$  zinc-blende structure and the  $\gamma$ -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 °C) as  $S^{2-}$  source being relatively high, a solvothermal reaction in lower temperature conditions (60–130 °C) using different precursors (thioacetamide and  $Mn(CH_3COO)_2$ ) and water as solvent has led to the formation of the  $\gamma$ -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  $(A'A_3)B_4O_{12}$  exhibit interesting physical properties (magnetism, low-field magnetoresistance, etc.) [12].  $CaCu_3Mn_4O_{12}$  and other compounds of the  $(A'A_3)B_4O_{12}$  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  $CaCu_3Mn_4O_{12}$  were prepared at a lower pressure (2 GPa) in the same temperature domain ( $\approx 1000^\circ C$ ) 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 $LaCuO_3$ 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,  $LaCuO_3$  with the perovskite structure and metallic behavior,  $La_2CuO_4$  and  $CuO$  were used as precursors [17]. Recently, in order to investigate electronic properties of  $Cu^{3+}$  in such a  $LaCuO_3$  lattice through Mössbauer spectroscopy, it was necessary to dope  $LaCuO_3$  lattice with 1%  $^{57}Fe$ .

With  $La_2CuO_4$  and  $CuO$  [doped with  $^{57}Fe$  (1%)] as precursors, and the same experimental conditions that were used for the undoped material (6 GPa,  $950^\circ C$  in the presence of  $KClO_3$  as an oxygen source) no pure  $Cu^{3+}$  perovskite was observed.

The preparation of the  $^{57}Fe$ -doped  $LaCuO_3$  required two steps: (i) the reaction between the precursors and (ii) the copper oxidation ( $Cu^{2+} \rightarrow Cu^{3+}$ ). A new precursor,  $La_2Cu_2O_5$ , was selected in order to reduce the preparation process to the second step.  $La_2Cu_2O_5$  can adopt two different structural forms: orthorhombic [19] and monoclinic [20].  $LaCu_2O_5$  (doped with  $^{57}Fe$  (2%)) was prepared with the two structural forms. Using oxygen pressures in a Walker-type module apparatus (using  $KClO_3$  as oxygen source), only the orthorhombic form is transformed to pure  $LaCuO_3$ : 1%  $^{57}Fe$  (11.5 GPa,  $900^\circ C$ ) [21]. Such a result can be explained through the specific structure of the orthorhombic form  $La_2Cu_2O_5$  isomorphous with  $Ca_2Mn_2O_5$ .  $Cu^{2+}$  occupying a  $(CuO_5)$  square pyramid in such a structure. The transformation ( $La_2Cu_2O_5$ :  $^{57}Fe \rightarrow 2 LaCuO_3$ :  $^{57}Fe$ )

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  $\text{La}_2\text{Cu}_2\text{O}_5$ :  $^{57}\text{Fe}$  with a monoclinic structure, characterized by two different  $\text{Cu}^{2+}$  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  $\Delta V$  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.

## References

- [1] J.B. Goodenough, J.A. Kafalas, and J.M. Longo, *Preparative methods in solid state chemistry*, in *High Pressure Synthesis*, P. Hagenmuller, ed., Chapter 1, Academic Press, New York, London, 1972.
- [2] G. Demazeau, H. Huppertz, J.A. Alonso, R. Pottgen, E. Moran, and J.P. Attfield, *Materials chemistry under high pressures – some recent aspects*, *Z. Naturforsch. B* 61(12) (2006), pp. 1457–1470.
- [3] P.F. McMillan, *High pressure synthesis of solids*, *Curr. Opin. Solid State Mater. Sci.* 4 (1999), pp. 171–178.
- [4] V.Z. Brazhkin, *High pressure synthesized materials: treasures and hints*, *High Press. Res.* 27 (2007), pp. 333–351.
- [5] G. Demazeau, *Solvothermal reactions: an original route for the synthesis of novel materials*, *J. Mater. Sci.* 43 (2008), pp. 2104–2114.
- [6] P. Reig, *Les phyllosiloxides: de nouveaux matériaux d'interphase lamellaires tout-oxyde pour matériaux composites*, No. d'ordre: 1226, Université Bordeaux 1, 1995.
- [7] P. Reig, G. Demazeau, and R. Naslain, *A new class of bidimensional oxides: the phyllosiloxides*, *Eur. J. Solid State Inorg. Chem.* 32 (1995), pp. 439–456.
- [8] P. Reig, G. Demazeau, and R. Naslain, *KMg<sub>2</sub>AlSi<sub>4</sub>O<sub>12</sub> phyllosiloxide as potential interphase material for ceramic matrix composites. Part 1: chemical compatibility*, *J. Mater. Sci.* 32 (1997), pp. 4189–4194.
- [9] V.V. Brazhkin, *Metastable phases and “metastable” phase diagrams*, *J. Phys.: Condens. Matter* 18 (2006), pp. 9643–9650.
- [10] J. Lu, P. Qi, Y. Peng, Z. Meng, Z. Yang, W. Yu, and Y. Qian, *Metastable MnS crystallites through solvothermal synthesis*, *Chem. Mater.* 13 (2001), pp. 2169–2172.
- [11] Y.C. Zhang, H. Wang, B. Wang, H. Yan, and M. Yoshimura, *Low-temperature hydrothermal synthesis of pure metastable  $\gamma$ -manganese sulfide (MnS) crystallites*, *J. Cryst. Growth* 243 (2002), pp. 214–217.
- [12] H. Shiraki, T. Saito, T. Yamada, M. Tsujimoto, M. Azuma, H. Kurata, S. Isoda, M. Takano, and Y. Shimakawa, *Ferromagnetic cuprates  $\text{CaCu}_3\text{Ge}_4\text{O}_{12}$  and  $\text{CaCu}_3\text{Sn}_4\text{O}_{12}$  with A-site ordered perovskite structure*, *Phys. Rev. B.* 76 (2007), pp. 140403-1–140403-4.
- [13] J. Chenavas, J.C. Joubert, M. Marezio, and B. Bochu, *The synthesis and crystal structure of  $\text{CaCu}_3\text{Mn}_4\text{O}_{12}$ : a new ferromagnetic-perovskite-like compound*, *J. Solid State Chem.* 14 (1975), pp. 25–32.
- [14] J. Sanchez-Benitez, J.A. Alonso, H. Falcon, M.J. Martinez-Lope, A. De Andres, and M.T. Fernandez-Diaz, *Preparation under high pressures and neutron diffraction study of new ferromagnetic  $\text{RCu}_3\text{Mn}_4\text{O}_{12}$  ( $R = \text{Pr, Sm, Eu, Gd, Dy, Ho, Tm, Yb}$ ) perovskites*, *J. Phys.: Condens. Matter* 17 (2005), pp. S3063–S3068.
- [15] C.M. Sung and M.F. Tai, *Reactivities of transition metals with carbon: implications to the mechanism of diamond synthesis under high pressure*, *Int. J. Refract. Met. Hard Mater.* 15 (1997), pp. 237–256.
- [16] C.M. Sung, M.F. Tai, C.S. Cheng, Q.S. Huang, and Y.D. Yao, *Kinetics of the graphite to diamond transition under high pressures*, *High Temp.–High Press.* 27/28 (1995/1996), pp. 499–512.
- [17] G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Sur deux nouvelles phases oxygénées du cuivre trivalent:  $\text{LaCuO}_3$  et  $\text{La}_2\text{Li}_{0.50}\text{Cu}_{0.50}\text{O}_4$* , *Mater. Res. Bull.* 7 (1972), pp. 913–920.
- [18] J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, *Sur une nouvelle phase oxygénée du cuivre +III:  $\text{SrLaCuO}_4$* , *J. Solid State Chem.* 8 (1973), pp. 325–330.
- [19] K.R. Poeppelmeier, M.E. Leonowicz, J.C. Scanlon, J.M. Longo, and W.B. Yelon, *Structure determination of  $\text{CaMnO}_3$  and  $\text{CaMnO}_{2.5}$  by X-ray and neutrons methods*, *J. Solid State Chem.* 45 (1982), pp.71–79.

- [20] M. Karppinen, H. Yamauchi, H. Suematsu, K. Isawa, M. Nagano, R. Itti, and O. Fukunaga, *Control on the copper valence and properties by oxygen content adjustment in the  $\text{LaCuO}_{3-y}$  system ( $0 < y < 0.5$ )*, J. Solid State Chem. 130 (1997), pp. 213–222.
- [21] G. Demazeau, A. Baranov, G. Heymann, H. Huppertz, A. Sobolev, and I. Presniakov, *A novel preparation process for  $\text{LaCuO}_3$  involving a high pressure oxidation of precursor derived from the perovskite structure: an appropriate route for doping with  $^{57}\text{Fe}$  Mössbauer probe*, Solid State Sci. 9 (2007), pp. 376–379.