Synthesis of novel materials under high pressures

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Abstract

Through an analysis of the research works involving the high pressure synthesis of novel materials during these last 20 years, high pressures can be involving either as thermodynamical parameters or reactive component. These both aspects of high pressure synthesis can be developed roughly at two different scales: (i) the macroscopic one when a material (including composition and structure) is involved or (ii) the nanoscopic scale when pressure can modify some atomic parameters (size, electronic structure...).

The first approach involving a pressure domain more accessible (from 10 MPa to 20 GPa) using different equipments (reaction vessel, piston-cylinder, belt, multianvils...) and different reaction medium (gas, liquid, solid), was the most developed.

The second approach requiring high pressure values can be mainly developed through Diamond Anvil Cell.

In the near future two research areas seems to be promising: (i) the high pressures involving in addition a fluid phase (Solvothermal Reactions) due to the improvement of the reactivity and (ii) the materials chemistry in Diamond Anvil Cell.

Introduction

High pressures is a specific thermodynamical parameter compared to temperature = its large scale (from 10^{-32} to 10^{+32} bar) [1] and the energy converged-directly correlated to the compressibility of the involved medium.

The development of High Pressures being directly correlated to that of materials – in particular alloys – for building the appropriated equipments, such a parameter started to be use in the synthesis of novel materials at the beginning of the XX^{th} century [2].

Different equipments have been set up for improving the synthesis of novel materials under high pressure: the reaction vessel-type (P \leq 500 MPa), the piston-cylinder (1 \leq P \leq 3 GPa), the belt-type apparatus 1 \leq P \leq 10 GPa, the cubo-octahedral multi-anvils 2 \leq P \leq 2,5 GPa and

then the diamond-anvil-cell (D.A.C.) opening new limits to the highest pressures (50-100 GPa).

In the major cases the high pressure synthesis of novel materials requires – for improving the reactivity – the temperature.

In a first approach high pressure synthesis involve both macroscopic and nanoscopic phenomena versus the pressure range. The macroscopic phenomena concern mainly the behaviour a the reactants under high pressure conditions and/or the reactivity. The nanoscopic phenomena involve the compressibility of atoms and in the upper range of pressure modifications of their electronic structure.

For the first two different cases can be take into account: the reactive pressure (where pressure acts as reactant or improved the reactivity during a step) or the unreactive pressure where the thermodynamical effects are predominant.

I. High pressure synthesis of novel materials involving macroscopic phenomena

The following description summarizes the main domains involving the synthesis of novel materials.

I.1 Materials synthesis with no reactive pressure

I.1.1 Synthesis of materials through densification effect.

Roughly the synthesis of a resulting materials (M) from two reactants R_1 and R_2 is strongly dependent on the $\Delta V/Z$ values.

$$\begin{array}{cccc} R_1 & + & R_2 & \rightarrow & M \\ \\ V_1/Z_1 & & V_2/Z_2 & & V_3/Z_3 \end{array}$$

where V/Z represents the volume per unit formula for each reactant and for the resulting material. Pressure parameter can help the synthesis only if $(V_1/Z_1 + V_2/Z_2)$ is higher than V_3/Z_3 ($\Delta V < 0$).

Such a densification effect has been used for the preparation of different novel materials, Table I giving different examples. In some cases the high pressure synthesis leads to a denser structure than that observed in normal conditions, as an illustration: the synthesis of the MV_2O_6 phases (M = Ni, Mg; Co, Zn, Mn, Cd) with the orthorhombic columbite structure different than the brannerite-type structure observed at normal pressure conditions [3].

The negative ΔV value favors the synthesis of materials characterized by high coordination number for the corresponding cations. Consequently high pressure have been largely developed for preparing new compositions with the perovskite-type structure (for example the double-perovskites Pb₂(B,B')O₆ with B' = Zn, Fe Co, Mn and B = W, Mo) [4].

This phenomenon has been also used for the stabilization of Laves phases (MgCu₂-type) such as LaCo₂ or LnFe₂ (Ln = Pt, Nd, Yb) [5, 6].

Material	P, T conditions for the synthesis	Structure	Ref.
MV ₂ O ₆ (M=Ni,Mg,Co,Zn,Cd)	5-8 GPa 800-1200°C	Orthorhombic- columbite	[3]
Pb ₂ (B,B')O ₆ (B'=Zn,Fe,Co,Mn ; B=W,Mo)	1-3 GPa 850°C	Perovskite-type	[4]
LaCo ₂	1-6.5 GPa 1050-1350°C	MgCu ₂ -type	[5]
LnFe ₂	2-3 GPa 1000°C	MgCu ₂ -type	[6]

Synthesis of some materials under high pressure conditions through densification effect **Table I**

I.1.2 Synthesis of materials due to the stabilization of unstable precursors

As indicated before, for improving the reactivity, temperature is always used in high pressure synthesis of materials - mainly in solid state chemistry - with the absence of solvent or liquid phase.

Consequently in order to maintain the stoichiometry, it is necessary to prevent all modification of the chemical composition of the reactants in the temperature domain required for the synthesis.

Versus their thermal stability different materials are decomposed at a temperature T_d.

With the formation of a gas phase – in particular for the oxides: HgO, PbO_2 , MnO_2 [10, 11], high pressure - being unfavourable for such a gas phase - improves the temperature domain of stability of the involved unstable reactants.

Consequently the required pressure domain must is selected for increasing T_d over the reaction temperature domain T_M .

Such high pressure processes have been largely used from the first developments of high pressure synthesis of novel materials [7].

I.1.3 Synthesis of materials with mixed anions

In order to prepare materials with mixed anions, it is necessary to improve the reaction involving precursors with different physico-chemical properties.

This high pressure domain was firstly involving for preparing oxyfluorides as $TI^{T}I^{II}OF_{2}$ [8] and $KTiO_{2}F$ [9]. In the near future, it will be used for developing specific classes of materials as nitrofluorides due to the electronic equivalence ($2O^{2-} \equiv N^{3-} + F^{-}$) [10, 11, 12], nitrochlorides [13], fluorosulfides [14], oxysulfides...

I.1.4 Synthesis of materials with light elements involving strong covalent bonds

The physico-chemical properties of a material are strongly correlated to the interactomic distance A-B, the ionicity coefficient characterizing the A-B chemical bond and the structure.

Consequently materials with lights elements – in particular the 2p elements – have been developed from the first synthesis of diamond (superhard-materials).

In such a domain of synthesis high pressures improve the reactivity of the reactants. Different research axis has been (and are always) strongly investigated:

- the polymerization of fullrenes [15,16],
- the B-C-N system [17,18,19],
- the B-O system [20,21],
- the preparation of carbonitrides specially C₃N₄ [22-24],
- the Si-C-N system [25].

The reactivity of reactants involving light elements can be also improved through reactive pressure in particular the use of a liquid phase implying both flux-assisted reactions [26] or solvothermal reactions [27].

I.2 Synthesis of novel materials using reactive pressures

I.2.1 Solvothermal reactions

Solvothermal reaction can be described as a chemical reaction involving a solvent either in subcritical or super-critical conditions. Such a solvent can act as a chemical component or only as fluid phase able - through its physico-chemical properties - to modify the mechanisms of the corresponding reaction between the reactants.

Solvothermal reactions involve different pressure domains: from the autogeneous pressure to a pressure level close to 400 MPa. The main objective of such reactions is to set-up processes in mild conditions for preparing novel materials.

In particular three main areas are concerned:

- the preparation of material through geomimetism [28],
- the development of new processes for the stabilization of materials with light elements [In particular two materials are concerned: cubic BN [27, 29] and C₃N₄ [30]],
- the stabilization due to the mild temperature conditions of novel hybride materials involving organic and inorganic chemistry [31, 32].

I.2.2 Gaz reactive pressures

Two main gaseous compositions have been used for preparing novel materials under high pressures: oxygen and fluorine. In such a paper, oxygen pressure has been selected as illustration. In Solid State Chemistry, an important Challenge is to correlate the physical properties of the oxides versus the strength of the chemical bond. The covalency of the M-O bond depends on the "formal oxidation state" n+ of the transition metal M.

Consequently high oxygen pressures have been developed for the stabilization of the highest oxidation states of transition metals.

During these last thirty years high oxidation states in different structures have been investigated.

Element	Oxidation state	Electronic configuration	Oxide	Ref.
Cr	Cr(V)	$t_2^2 e_g^0$	La ₂ LiV _{1-x} Cr _x O ₆	[33]
Fe	Fe(IV)	$t_{2g}^3 d_{z^2}^1 d_{x^2 - y^2}^0$	A _{0.5} La _{1.5} Li _{0.5} Fe _{0.5} O ₄ A=Ca, Sr, Ba	[34]
			(SrLa)M _{0.5} Fe _{0.5} O₄ M=Mg, Zn	[35]
Fe	Fe(V)	$t_{2g}^3 e_g^0$	La ₂ LiFeO ₆	[36]
Со	Co(III)	LS →HS LS →HS	LnCoO₃ (Ln = La→Lu) SrLnCoO₄	[37] [38]
Со	Co(IV)	$t_{2g}^6 e_g^0$	(Sr _{0.5} La _{1.5})Li _{0.5} Co _{0.5} O ₄	[39]
Ni	Ni(III)	$t_{2g}^6\sigma^{*1}$	LnNiO₃ (Ln = La→Lu) SrLnNiO₄	[40] [41]
Cu	Cu(IV)	$\frac{t_{2g}^6 d_{z^2}^2 d_{x^2-y^2}^0}{t_{2g}^6 \sigma^{*2}}$	La ₂ Li _{0.5} Cu _{0.5} O ₄ LaCuO ₃ SrLaCuO ₄	[42] [42, 43, 44]
lr	lr(V)	$t_{2g}^4 e_g^0$	La ₂ LilrO ₆	[45]
lr	lr(∨I)	$t_{2g}^3 e_g^0$	Ba ₂ CalrO ₆	[46]

Stabilization of unusual oxidation states of transition metals of the first raw under high oxygen pressures **Table II**

More recently some studies have been developed for correlating the covalency of the $M^{n+}-O$ bond and the induced electronic phenomena [charge transfer ($M^{n+}-O^2 \Leftrightarrow M^{(n-1)+}-O\underline{L}$), disproportionation ($2M^{n+} \rightarrow M^{(n-1)+}+M^{(n+1)+}$), spin transition (as low-spin \rightarrow high spin)].

In particular during these last ten years a large interest has been developed on the study of low spin Ni³⁺ ($t_{2g}^{6}e_{g}^{1}$) oxides - in particular the TNiO₃ perovskites T=rare-earth. such a family of oxides presenting a large spectrum of electronic phenomena versus the electronic localization of the e_{g}^{1} electron [47-50].

II. High pressure synthesis of novel materials through nanoscopic phenomena

Two main phenomena are predominant: (i) the compressibility of the different atoms participating to the composition of the resulting material, (ii) the modification of the electronic structure of such atoms resulting of the compressibility.

II.1 Influence of the compressibility of atoms on the stabilization of materials

The structure adopted by a material is closely dependent on the respective size of the corresponding cations (A) and anions (B) (r_A/r_B) or cations (r_{A1}/r_{A2}) . For example, in the case of the $A_2M_2O_7$ 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 close to 1.8 in normal conditions. Due to the difference of compressibility between rare earth A^{3+} and Ge^{4+} it was possible under high pressure conditions to prepared the $A_2Ge^{4+}O_7$ series (A=rare earth) with the pyrochlore structure [51].

II.2 Modification versus pressure of the "in situ" cation-electronic configuration

The compressibility "in situ" of a cation can induce a modification of the orbitals-energy and consequently its electronic configuration.

The reactivity being dependent on such electronic configuration has allowed to develop a new research area at the highest pressures.

As an illustration for the alcaline earth, as K, Rb, Cs, the energy of the external s orbital increases strongly that the d orbitals, consequently for a specific high pressure level - the $s \rightarrow d$ transition - confers the character of transition metal.

If at ordinary pressure alcaline earths do not react with transition metal as nickel, however under very high pressures such alloys as K_3Ag and KAg_2 can be prepared [52].

Conclusions

High pressures appear an important tool for improving the development of novel materials with two different objectives: (i) the improvement of basic knowledge involving the correlations between physical properties and the characteristics of the materials (composition, chemical bond, structure...), (ii) the development of new mild processes in particular solvothermal ones for materials devoted to industrial applications.

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