



Hydrothermal synthesis for new multifunctional materials: A few examples of phosphates and phosphonate-based hybrid materials



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ABSTRACT

Novel physical or chemical properties are expected in a great variety of materials, in connection with the dimensionality of their structures and/or with their nanostructures, hierarchical superstructures etc. In the search of new advanced materials, the hydrothermal technique plays a crucial role, mimicking the nature able to produce fractal, hyperbranched, urchin-like or snow flake structures. In this short review including new results, this will be illustrated by examples selected in two types of materials, phosphates and phosphonates, prepared by this method. The importance of the synthesis parameters will be highlighted for a magnetic iron based phosphates and for hybrids containing phosphonates organic building units crystallizing in different structural types.

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1. Introduction

It is strongly recognized that transition metal oxides provide a huge playground in material science, due to their structures but also to their properties with applications in catalytic, magnetic, electronic devices etc. This richness is due to the adaptability of the structures which accept distortions, intergrowths, substitutions, non-stoichiometry in connection with several oxidation states – and thus electronic configurations – for one cation together with possible charge and/or orbital ordering. The combination of these parameters leads to complex and interesting phase diagrams (*versus* composition) or phase transitions (*versus* temperature). These compounds are usually gathered in classes of materials, like transition metal oxides (perovskites, Ruddlesden–Popper phases), silicates, borates or phosphates to mention a few types of inorganic-based materials. The incorporation of organic molecules to produce crystalline materials offers other classes of compounds also identified as Metal Organic Framework (MOF), hybrid materials or coordination polymers. Each type of materials, oxides or hybrids, has its own community of chemists and involves different methods of synthesis, but the gap between these two words is coming closer as soon as applications are considered (for magnetic, catalytic or medical devices for examples). A common

problematic to both types of materials is the production of well crystalline samples with an adapted size of crystallites to address for instance, the characterization of some physical properties, as magnetic anisotropy, electrical resistivity and polarization, electrochemical properties etc.

More often, synthesis modes are adapted in order to obtain optimized properties and adequate shape of samples, as highly compact ceramics for electrical characterizations, control of the compositions to monitor magnetic properties or of the microstructure and size of the nanoparticles for catalytic applications. The choice of the preparation techniques depends thus on the composition and desired properties; on the contrary, sometimes particular techniques allow stabilization of unexpected compounds. In addition, multistep processes – as intercalation or topotactic exchange – may be undertaken to stabilize new compounds. After a short section dealing with generalities about the technique, we will illustrate by a few examples the influence of the hydrothermal synthesis conditions on the structure of the obtained phosphates and phosphonates-based hybrid and on their crystallinity.

2. A few points relating to hydrothermal synthesis

A famous case of studies inspired by the way the nature proceeds is the well-known example of hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$

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which remains always of great interest since the pioneer reports dealing with its structure in 1964 [1]. Nowadays, due to potential applications, numerous works are devoted to the control of the shape of the particles that is strongly influenced by pH, precursors used and their amounts, time, reaction temperature [2–4], by the saturation of the reaction system [5] etc. Moreover, the preparation of asymmetric micro and nano-particles has been explored by searching for different strategies and fabrication process in order to "reproduce" the existing particle formats in nature [6,7] since nano/micro-structure, porosity, surface quality are key parameters for imaging promising devices particularly for medical purposes [8].

Quite simply for one technique, varying some parameters may induce strong differences in the obtained samples and we propose here to focus on hydrothermal technique for preparing either phosphate-based oxides or phosphonate-based hybrid materials. We selected a few examples among our work to illustrate the topic without claiming to be exhaustive. According to hydrothermal synthesis, the reactions are carried out in water in a Teflon reactor liner in which the precursors are introduced in the desired proportions. These reactors are then placed in steel autoclaves to be heated by conventional means (Joule effect) or directly introduced into a microwave oven. The thermal cycles and synthesis temperatures are then adapted according to the first results obtained. Four main types of reactants should be considered and distinguished: the solvent, the nature of the inorganic precursors, the organic precursors and the use of base or mineralizing agents. Metal phosphates or phosphonates are mostly synthesized in aqueous solvent (the term hydrothermal process is then used) or in organic solvent like DMF, DMSO, methanol (solvothetical process). The use of ionic liquid, initially introduced by the group of Morris, constitutes an additional possible condition leading to the terminology of ionothermal synthesis [9]. By playing with the nature of the solvent, it is possible to change the polarity, solubility of the precursors, ebullition point or pH of the media in order to increase the crystallinity of the obtained materials. The precursors can be dissolved in the same time or sequentially, they are inorganic salts like metal acetate, metal nitrate or metal halide and organic molecules bearing one or more reactive functions like carboxylate, sulfonate or phosphonate (different in types and numbers). The reactivity of these functions can be increased by using basic media which is obtained by the addition of KOH, NaOH or urea $(\text{NH}_2)_2\text{C}=\text{O}$. These conditions impact the kinetic of the reaction and likely also the crystallinity of the materials.

2.1. From phosphates to phosphonates

The starting point of the iron phosphates study was the preparation of compounds, stabilizing Fe^{+2} and Fe^{+3} species, looking for multiferroic properties that can be induced by charge ordering and/or complex magnetic structures. It is well known that divalent iron is difficult to stabilize but it exists in numerous minerals. Even if, more often, compositions are not well defined in natural samples, the abundance of such compounds proves the interest of hydrothermal synthesis for this topic. Moreover, in a general manner for magnetic materials, there are strong correlations between magnetic properties and nanostructures, whose understanding is still under debate [10]. As an example, in Fe_2O_3 i.e. a compound containing only trivalent iron, shape dependent magnetic properties have been reported, with a direct impact on the Morin transition varying from 251 K to 221 K, in ellipsoid and rhombohedra shaped α - Fe_2O_3 samples, respectively [11].

Phosphonate-based hybrid materials can also be synthesised under hydrothermal conditions. These conditions are nowadays routinely used in order to produce crystalline samples and to improve the crystallinity of materials. It is worth noticing that other strategies were first employed to produce crystalline metal-

phosphonate materials. Alberti et al. [12] used strongly acidic conditions (HF) to prepare zirconium phosphonate materials. ZrF_6^{2-} is likely one quite stable intermediate specie which reacts slowly with phosphonic acid, explaining thus the good crystallinity of the final material. However the use of HF is not always adapted and for evident safety reasons alternative to the use of HF was welcome. With the aim to observe a slow crystallization process we have reported the synthesis of zirconium phosphonate directly from diethyl or dimethylphosphonate, instead of phosphonic acid, in acidic conditions. In that case the use of high concentration of acid (e.g. HCl) deeply improves the crystallinity of the samples but only crystalline powder was isolated [13]. Hydrothermal synthesis constitutes an alternative method to produce crystalline samples but it must be noted that many experimental procedures may be necessary until finding the optimal conditions to produce crystals of adapted size. These parameters, to mention the most important, are temperature, time of synthesis, thermal cycle, nature and concentration of the precursors (salt, organic molecules), nature of the solvent, pH of the reaction media. However, without giving herein too many details because these points have already been widely discussed in the literature [14–16], we will briefly recall some significant parameters specific to this type of crystal growth.

3. Selected examples of materials

3.1. From phosphates...

In a first example, we would like to illustrate the consequence of the synthesis conditions on the structure of an iron-phosphate material, in connection with the existence of allotropic forms. Indeed, two kinds of structures are reported for the mixed-valent iron ammonium phosphate $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ synthesized using different temperature and pressure conditions, starting from different precursors [17,18]. The α -form was first prepared using high-*T* and high-*P* hydrothermal synthesis (500 °C and 2200 bar), starting from a mixture of $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, Fe_2O_3 and water in a sealed gold ampoule [17]; a few years later, β - $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ was obtained using low-*T* and low-*P* hydrothermal process [18], starting from Fe_2O_3 , FeCl_2 , $(\text{NH}_4)_2\text{HPO}_4$ and water in a Teflon-lined stainless steel autoclave. α and β - $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ structures are very close, both being characterized by chains of edge-sharing Fe^{+2}O_6 octahedra and chains of corner-sharing Fe^{+3}O_6 octahedra and PO_4 tetrahedra, but differ by the presence of a complex structural disorder in the β -form. Although both structures are very similar, it is possible to distinguish α from β by X-ray diffraction. We report here for the first time that a polycrystalline sample of the α -form can also be synthesized by hydrothermal method at lower *P* and *T* conditions: i.e. at ≈ 60 bar and 250 °C in a Teflon-lined steel autoclave, starting from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (2.5 M), Fe_2O_3 (1.25 M), $\text{NH}_4\text{H}_2\text{PO}_4$ (4 M) and $\text{C}_6\text{H}_8\text{O}_4 \cdot \text{H}_2\text{O}$ (1 M) at pH=4 (by adding the necessary amount of ammonia). Moreover, needle like single crystals of the β - $\text{NH}_4\text{Fe}_2(\text{PO}_4)_2$ form were obtained using high-*T* and high-*P* hydrothermal synthesis (400 °C, 322–430 bar), starting from $\text{NH}_4\text{H}_2\text{PO}_4$, Fe_2O_3 and FeO . The X-ray diffractograms of these crushed as-synthesized samples and their morphologies are shown in Fig. 1 (and inset). This example of two allotropic forms that can both be obtained using high or low *T* and *P*, with different precursors, clearly evidences the difficulties that can be encountered to manage the crystal growth of such materials and to analyze the influence of the different parameters during hydrothermal synthesis.

Nevertheless, the possibility to control some characteristics, such as the size and/or shape of particles, has been demonstrated for several iron phosphates, as the control of the morphology of

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