HYDROTHERMAL PRODUCTION AND DEVELOPMENT OF MATERIALS
BASED ON COMPUTER SIMULATIONS FROM THERMODYNAMIC DATA

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ABSTRACT

Thermodynamic simulations can be performed nowadays in all areas of materials processing due to the advances that have been taken place in computer software for complex non-ideal calculations, together with the increasing availability of evaluated data for phases of different types. In the present work, a thermodynamic model of electrolytic solutions was applied to determine the reaction conditions favoring the hydrothermal synthesis of zinc ferrites and sodium niobates. Stability and yield diagrams were constructed relating the equilibrium concentration of all the aqueous and solid species as functions of temperature, pressure, pH, and input reagent concentrations. The theoretical predictions avoided the empirical "trial-and-error" mode of synthesis and were further corroborated by experiments. The results demonstrated the important role that such thermodynamic simulations play in significantly reducing the time and costs associated with the hydrothermal processing.

INTRODUCTION

With the beginning of the 21st century, it is time to understand that there is a strong relationship between economic growth and progress in materials science. It was estimated that this branch of science contributes directly or indirectly to some 30-40% of the Gross Domestic Product in developed countries, through processes and products, including electronic, photonic, ionic, magnetic, optical, ferroelectric, piezoelectric, semiconductor, superconductor, insulator, varistor, sensor, luminescent, catalytic and environmental materials (Férey and Jacobson, 1999). The continuously increasing demand from industry for tailored materials for specific applications leads materials scientists to improve the performance of known systems and to create new solids with enhanced properties. This challenge provides a driving force for innovation, discovery of new phases and for new techniques and approaches to chemical synthesis.

From the beginning of the fifties, synthesis in materials science was mainly associated with reactions at high temperatures and/or pressures. The conventional powder processing, for example, involved several steps including high temperature calcination, milling, and sintering to produce a final ceramic body. All these steps are highly energy consuming and thus have resulted in environmental problems. The introduction in the eighties of the concepts of "chimie douce" or soft solution processes opened the way for new pathways including low temperature reactions and the use of solutions (Matsumoto, 1998). Solubilization and precipitation phenomena combined with acid-base and redox chemistry allow the development of new inorganic or hybrid inorganic-organic materials in which organic species can be introduced as reactants. Compared with solid-solid reactions where diffusion processes govern the nature of the product, solution media allow different approaches to the synthesis and modification of solids.

Hydrothermal synthesis is frequently used for preparing materials for a variety of applications (Yoshimura, 1998). The desired products can be obtained from either a homogeneous phase or through heterogeneous reactions between aqueous species and solid reactants suspended in solution. Among the materials that can be obtained by using this procedure, microporous, mesoporous and low dimensional solids have become of importance in catalysis, separations and environmental applications. The hydrothermal processing works with closed-flow systems, which makes easy any charging, separation, cycling and recycling; allows a relatively high deposition rate; and presents the lowest one total energy consumption among all aqueous solution-processing routes (Matsumoto, 1998).

Usually, the development and optimization of materials and processes are time-consuming, which means high costs. For this reason, computer simulations from theoretical existing thermodynamic data are nowadays increasingly employed for materials
production and development (Spencer, 1999). The field of modeling and simulation in materials science and engineering is extremely broad and even for a single year the number of papers published is in the thousands. Recently, theoretical simulations of the hydrothermal conditions on ceramic systems were conducted by using computer software developed by OLI Systems, Inc., to model aqueous, conventional and other complex chemical phenomena (Lencka et al., 1997). These include interphase equilibrium, intraphase equilibrium in redox and speciation reactions, chemical reactions, reactions kinetics, ion exchange and co-precipitation (Anderko et al., 1997). The software (Corrosion and Environmental Simulation Programs) provides a refined user interface, which includes an advanced thermodynamic framework as basis for predicting complex aqueous-based chemistry in equilibrium with vapor and solid phases at temperatures in the range 0-300°C, pressures up to 1500 bar and molal ionic strength in the range 0-30m. Also, an extensive thermodynamic and physical property database verified and validated from source literature is employed (Zemaitis Jr. et al., 1986; Rafal et al., 1995).

OLI uses a highly advanced thermodynamic and mathematical framework for predicting the equilibrium properties of a chemical system based upon the revised Helgeson equation of state (Oelkers and Helgeson et al., 1993) for predicting the standard state thermodynamic properties, the Bromley-Zemaitis model for the prediction of ion-ion interactions, and the Pitzer-Setschenow formulation for the analysis of the thermodynamic properties in calculations involving ion-molecule and molecule-molecule interactions in water (Anderko et al., 1997). Besides, the enhanced Soave-Redlich-Kwong equation of state (Anderko et al., 1997) for the prediction of vapor and liquid phase thermodynamic properties (fugacity coefficients) is used. The approach accounted the effects of long-range electrostatic forces as well as the short-range forces by parameterization of the virial coefficients. The Pitzer treatment of the aqueous model is based on equations proposed by Harvie et al. (1984) The most significant here is the fundamental information provided for non-ideal conditions. This often gives new insight into the basis of compositional and phase changes in complex systems under different process conditions (Anderko et al., 1997).

In previous works (Ciminelli and Dias, 2000; Dias and Ciminelli, 2001), we discuss the formation of strontium and nickel tungstates under hydrothermal controlled conditions. In this work, experimental procedures for the hydrothermal synthesis of ZnFe₂O₄ (Franklinite) and Na₂SnO₄ were developed with basis on thermodynamic simulations. For these aqueous systems, chemistry models were created after listing the molecular species involved in the hydrothermal processing simulations. The software automatically generated a detailed speciation (ionic species in the aqueous solution), the interphase and aqueous speciation equilibrium reactions and the required physical and thermodynamic property information for a particular mix of chemicals involved. The electrolyte solution model used is able to simulate the chemical reactions in hydrothermal systems under a wide range of temperatures, pressures, reagent input concentrations and chemical environments (Lencka et al., 1997; Anderko et al., 1997). The theoretical predictions were corroborated by experimental results and minimized the empirical trial-and-error synthesis. Hydrothermal syntheses were conducted according to the theoretical predictions at different conditions of temperatures, pH and input reagent concentration, under saturated vapor pressure. The aqueous solutions containing the reactants and at a pH value previously established were loaded into stainless steel Parr® autoclaves (Model 4532) equipped with turbine-type impellers and occupied about 50% of the total volume of 2000 mL. The autoclaves were heated at 4°C.min⁻¹ up to the processing temperature and maintained there for 4 hours. After synthesis, the powders were repeatedly washed with deionized water (18,2 MΩ.cm) in order to remove any remaining Na⁺ ion and dried in an oven at 80°C. X-ray diffraction (Philips PW1830, Ni-filtered CuKα radiation, 40kV, 20mA), X-ray fluorescence (Philips PW2400 sequential spectrometer, Rhodium target end window, Super Q analytical software), and atomic absorption spectrometry (Perkin Elmer 5000) were employed in the structural and chemical characterization.

**HYDROTHERMAL PRODUCTION AND DEVELOPMENT OF ZINC FERRITES**

The hydrothermal production of AB₂O₄ ceramics, particularly metal ferrites, was extensively studied in our laboratory. The main results were published elsewhere for different compounds, being their properties studied in detail (Dias and Buono, 1997; Dias et al., 1998; Dias and Moreira, 1999). In the present work, the hydrothermal synthesis conditions under which the phase-pure ZnFe₂O₄ can be produced were predicted by thermodynamic calculations of the Gibbs free energies for the balanced relevant reactions in water as functions of pH, input reagent concentrations and temperature/pressure. The results of the theoretical simulations are showed in the Figures 1 and 2 for the ZnFe₂O₄ produced from zinc sulfate hexahydrate and...
ferrous sulfate heptahydrate, which were chosen due to their high solubility in water. Sodium hydroxide and sulfuric acid were added when necessary in order to control the pH value. Hydrogen peroxide was also considered in the computer simulations as an oxidizer agent of the ferrous ions to produce the desired ferrite.

Figure 1 presents yield diagrams, which show the domains of relevant aqueous species and solid compounds at a given temperature or pressure. Two kinds of boundaries are illustrated in the diagrams: those between two aqueous species (dotted lines) and those between a solid and an aqueous species (solid lines). Also, yield diagrams display the fraction (yield) of product (ZnFe$_2$O$_4$) as a function of pH and the input concentrations of zinc, iron and hydrogen peroxide as a shaded area inside the ferrite stability region. Diagrams for ZnFe$_2$O$_4$ were obtained through computer simulations at 110°C (Fig 1a) and 230°C (Fig. 1b) for a yield=99% and concentration ratio [Zn]=[H$_2$O$_2$]=[Fe]/2=1.0 (the potential can vary along the concentration and pH values). It was observed that zinc ferrites can precipitate through a wide pH range in temperatures as low as 110°C (Fig. 1a) and input reagent concentrations as low as 10^{-6}m (Fig. 1a). As the reagent concentration decreases, the pH range where ZnFe$_2$O$_4$ could be obtained also decreases. For example, hydrothermal syntheses of this compound requires the feedstock pH values in the range 5.5-13.0 at 110°C (Fig. 1a) and 5-14 at 230°C (Fig. 1b), for an input reagent concentration equal to 1m. Reactions conducted out of the yield areas result in formation of undesirable metastable phases, unreacted or contaminating phases (e.g., magnetite or Fe$_3$O$_4$). The theoretical chemistry model considered for the calculations purpose the presence of other and undesirable phases like natrojarosite, wustite, NaFeO$_2$ and ZnO. The results showed that under the hydrothermal conditions studied these phases cannot be found.

Comparing the yield diagrams displayed in Figure 1, it can be seen a pronounced change in the phase boundaries in the pH range between 5 and 10. A decrease in the stability region of the aqueous specie Fe$^{2+}$ can be observed when the temperature increased from 110°C to 230°C, while the phase boundary between the aqueous species Fe(OH)$_2$ and Fe(OH)$_3$ shifted to lower pH values. Also, the aqueous specie Fe(OH)$_2$ was changed by the species Fe(OH)$_3$ at pH values between 6 and 8. An important change occurred in the acidic region as the hydrothermal temperature increased: the tremendous increase of the stability fields of the solid species hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) were verified and can be associated to the lower stability and yield of the solid phase ZnFe$_2$O$_4$. It is necessary to emphasize that at 110°C the minimum input concentration for the formation of zinc ferrites is really low (10^{-6}m), although the pH range for the ZnFe$_2$O$_4$ precipitation is narrow (8.5-9.5). Finally, it can be observed that the decrease on the stability and yield regions of ZnFe$_2$O$_4$ could be due to the increase of the stability of Fe(OH)$_2$ (completely stable at 230°C and pH>12 in practically all reagent concentrations) associated with the decrease on the stability regions of Fe$^{2+}$ (low pH values).

The results of the theoretical study of the influence of the hydrothermal conditions on the precipitation of zinc ferrites were corroborated by experiments. Table I displays the hydrothermal temperatures and input reagent concentrations predicted by computer simulations, as well as the phases experimentally observed. It was assumed a product amount ranging from 0.005 to 5mol/kgH$_2$O, either through the region of incomplete reaction (or outside yield area) as well as inside the yield areas displayed in Figure 1. Also, Eh-pH diagrams were constructed in order to better study the experimental conditions. Figure 2 presents these diagrams obtained at 110°C and 230°C for identical
hydrothermal conditions inside the ZnFe$_2$O$_4$ yield area 
\( \log [\text{Zn}] = \log [\text{H}_2\text{O}] = \log [\text{Fe}]/2 = -2.5 \). As verified by Dias and Buono, (1997), the chemical reactions involving the precipitation of metal ferrites in aqueous solutions can be generalized as follows:

\[
xM^{2+} + (3-x)Fe^{2+} + 6(\text{OH})_{(aq)} = M_xFe_{3-x}[(OH)_{6})_{(s)},
\]

\[
M_xFe_{3-x}(OH)_{6})_{(s)} + \frac{1}{2}O_2_{(g)} = M_xFe_{3-x}O_4(s) + 3H_2O(_l).
\]

The current experimental findings are consistent with thermodynamic predictions based on yield diagrams. As expected, the reactions between zinc and ferrous sulfates performed in the complete yield region of ZnFe$_2$O$_4$ produced phase-pure ceramics with low impurity levels (<0.5% wt., mainly Na, Ca, Pb and Ba), according to X-ray diffraction and chemical analyses. Ferrites produced under hydrothermal conditions outside the yield areas were obtained in a lower amount probably due to the dissolution of the starting materials. Also, magnetite was also observed in these outside yield regions in samples especially synthesized at 230°C. Appreciable amounts of sodium sulfate were found in lower hydrothermal temperatures, probably due to the smaller particle sizes of the ferrite powders obtained, which difficult the separation ferrite/Na$_2$SO$_4$, since the powder was in suspension in the liquid phase. No traces of hematite (Fe$_2$O$_3$) were found in the samples, as expected by the theoretical predictions.

Table 1 - Hydrothermal conditions employed for the synthesis of ZnFe$_2$O$_4$, as theoretically predicted, and experimental phases observed through X-ray diffraction.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>$\log [\text{H}_2\text{O}] = [\text{Zn}] = [\text{Fe}]/2$ (mol/kg H$_2$O)</th>
<th>$\log [\text{NaOH}]$ (mol/kg H$_2$O)</th>
<th>Phases</th>
<th>X-Ray diffraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>-2.5 ($^*$)</td>
<td>-1.5</td>
<td>ZnFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>-1.1 (I)</td>
<td>-0.3</td>
<td>ZnFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>-2.2 (O*)</td>
<td>-0.3</td>
<td>ZnFe$_2$O$_4$ + Na$_2$SO$_4$</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>-1.0 (O)</td>
<td>-1.5</td>
<td>ZnFe$_2$O$_4$ + Na$_2$SO$_4$ + Fe$_3$O$_4$</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>-2.0 (O)</td>
<td>-0.8</td>
<td>ZnFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>-2.5 (I)</td>
<td>-1.5</td>
<td>ZnFe$_2$O$_4$</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>-2.0 (O)</td>
<td>-0.3</td>
<td>ZnFe$_2$O$_4$ + Fe$_3$O$_4$</td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>-2.5 (O)</td>
<td>-0.5</td>
<td>ZnFe$_2$O$_4$ + Fe$_3$O$_4$</td>
<td></td>
</tr>
</tbody>
</table>

* $^*$ = inside yield boundary and O = outside yield boundary

**Figure 2** – Eh-pH diagrams obtained for input metal concentrations equal to $[\text{Zn}] = [\text{Fe}]/2 = 0.00316m$ at 110°C (gray lines) and 230°C (black lines). The dotted lines denote the stability field of water.

**HYDROTHERMAL PRODUCTION AND DEVELOPMENT OF SODIUM NIOBATES**

$ABO_3$ compounds are known as perovskites, whose applications include capacitors, thermistors, sensors and actuators. The atomic arrangement in the $ABO_3$ structure could be represented by $A$ atoms at the corners of a cube with $B$ atoms at the body center and oxygen ions at the center of the faces. For this category of electroceramics, we will exemplify the potential of the hydrothermal method to produce different crystalline phases in the system Na-Nb-H$_2$O depending upon the processing conditions employed. Sodium niobate (NaNbO$_3$) is a dielectric material of the perovskite group with a series of technologically important structural phase transitions between 200°C and 640°C (Megaw, 1974). In this work, sodium hydroxide and niobium chloride were employed as reactants in the computer simulations. It was observed that cubic sodium niobate (Lueshite-type) could only be produced at temperatures below 100°C. The increase in the hydrothermal temperature favored the stabilization of the phase Nb$_2$O$_5$ (niobium oxide) especially in higher input reagent concentrations, which diminished the yield for NaNbO$_3$. The fact that cubic NaNbO$_3$ can be produced at temperatures as low as 25°C means that an open vessel can be employed. Figure 3 presents the sodium niobate yield diagram obtained from simulations at room temperature and a concentration ratio Na/Nb=1.0. As it can be seen, the perovskite can be obtained through a wide pH range and reagent concentrations. The aqueous species HNbO$_3$ and NbO$_3$ are also present; niobium oxide can occur only at low pH values and very high reagent concentrations. As the hydrothermal temperature
increases, the stability of sodium niobate diminishes as well as the stability of Nb$_2$O$_5$ increases.

Figure 3 – Computer simulated yield diagram for the NaNbO$_3$ obtained at 25°C (Na/Nb ratio equal to 1.0).

After computer simulations, hydrothermal syntheses of NaNbO$_3$ were conducted in temperatures varying between 80 to 240°C, under saturated vapor pressure. Aqueous solutions of sodium hydroxide and niobium chloride were employed as reactants in the experiments. Table II presents the crystallographic information about the phases observed in the present work as a function of the reaction temperature. It was observed that the crystallographic phases changed drastically as the hydrothermal temperature increased. Low temperatures (80°C) favored the formation of cubic sodium niobates (Lukshte-type), while a mixture of cubic Na$_2$NbO$_4$ and NaNbO$_4$$_7$ was observed at 110°C. The increase in the hydrothermal temperature prompted the stabilization of the cubic Na$_3$NbO$_4$, leading to the total disappearance of the phase NaNbO$_4$$_7$ at 160°C. Two different phases were detected at 200°C: NaNbO$_4$$_8$ and monoclinic NaNbO$_3$ (Natroniobite-type). Finally, at 240°C, we have detected the presence of NaNbO$_4$$_8$ together with two other NaNbO$_3$ structural phases: orthorhombic and rhombohedral.

The reaction mechanisms and sequences that lead to particle formation in hydrothermal conditions include dissolution and re-crystallization of any solid precursor phase, dissolution of soluble species in solution, adsorption at the solid-liquid interface, and surface reaction followed by incorporation of solute materials into the lattice (Randolph and Larson, 1988). In the present work, it was observed that either solid phases or aqueous phases can be predicted by using computer simulations. The final product formed and its crystallinity as well as its morphological properties are complex functions of processing conditions (Dias and Buono, 1997). If metastable, it will eventually be transformed into something else, often in a series of steps. Its reactivity is governed by a set of thermodynamic and kinetic factors, and is generally higher than that of well-crystallized stable materials. Even for kinetically controlled processes, the direction of transformation is determined by, and the rate influenced by, the overall energy and free energy changes associated with the transformation among a succession of metastable states. Without knowledge of thermochemical properties one does not even know which reaction directions are possible.

Table II - Phases found throughout this study as a function of hydrothermal temperature.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Crystallographic Phases</th>
<th>ICDD card</th>
</tr>
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<tbody>
<tr>
<td>80</td>
<td>NaNbO$_3$ (cubic Lukshte)</td>
<td>19-1221</td>
</tr>
<tr>
<td>110</td>
<td>Na$_2$NbO$_4$$_7$</td>
<td>21-1149</td>
</tr>
<tr>
<td>160</td>
<td>NaNbO$_4$</td>
<td>22-1391</td>
</tr>
<tr>
<td>200</td>
<td>NaNbO$_4$$_8$</td>
<td>13-0330</td>
</tr>
<tr>
<td>240</td>
<td>NaNbO$_3$ (Natroniobite)</td>
<td>26-1380</td>
</tr>
<tr>
<td></td>
<td>NaNbO$_4$$_8$</td>
<td>13-0330</td>
</tr>
<tr>
<td></td>
<td>NaNbO$_3$ (orthorhombic)</td>
<td>33-1270</td>
</tr>
<tr>
<td></td>
<td>NaNbO$_3$ (rhombohedral)</td>
<td>37-1076</td>
</tr>
</tbody>
</table>

CONCLUSIONS

The advances in computer software for complex non-ideal calculations, together with the increasing availability of evaluated data for solution phases, allow conduct reliable thermodynamic simulations and to perform materials processing and development. In combination with a minimal-measurement program, the calculations permit rapid and reliable progress to be made that resulting from the combination of empiricism, experience, and a general knowledge of basic principles that is still frequently used as the basis for much materials-development work. Zinc ferrites as well as sodium niobates were chosen to study the influence of the hydrothermal conditions on the phase behavior. Single-phase and impurity-free ZnFe$_2$O$_4$ powders were obtained for hydrothermal conditions inside the yield areas theoretically predicted. Low ZnFe$_2$O$_4$ yields and other undesirable phases (like Na$_2$SO$_4$ and Fe$_2$O$_4$) were found after syntheses conducted outside the yield areas. For the pervoskite system Na-Nb-H$_2$O, it was observed a mixture of phases at temperatures higher than 110°C. Cubie NaNbO$_3$ can only be produced at temperatures below 100°C, while orthorhombic and rhombohedral NaNbO$_3$ phases were observed at 240°C.
ACKNOWLEDGEMENTS

The authors acknowledge the financial support from FAPEMIG, RHAE, CNPq and PRONEX.

REFERENCES


