

# Thermoanalytical study of iron(III) phosphate obtained by homogeneous precipitation from different media

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## Abstract

Amorphous iron(III) phosphate has been synthesised by homogeneous precipitation from equimolecular  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  aqueous, water–ethanol and water–*iso*-propanol solutions at  $\text{pH} = 2.0$  and ambient temperature using hydrogen peroxide as precipitating agent. The precipitates have been characterised by TG/DTG/DTA techniques, chemical analysis, X-ray powder diffraction (XRD) analysis and scanning electron microscopy (SEM). The presence of ethanol and *iso*-propanol in the precipitation medium suppressed the co-precipitation of ferric sulphate as it does in aqueous medium. Thermal treatment of the as-precipitates at  $750^\circ\text{C}$  in air yields a crystalline quartz-like structured  $\text{FePO}_4$  with markedly different morphological features.

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**Keywords:**  $\text{FePO}_4$ ; Thermal analysis; X-ray powder diffraction; SEM

## 1. Introduction

Iron(III) phosphate is recently gaining more and more interest as material to be used in the field of catalysis [1], wastewater purification systems [2], ferroelectrics [3], and lithium batteries [4,5]. Particularly in the field of lithium batteries it is used as cathode electrode or as precursor for phosphate-based anode electrodes. However, the successful of applicability of this material depends on the morphology and purity of the material. Powders obtained by the generally “high temperature” methods induces in fact the sintering and aggregation of particles, which are deleterious for the electrochemical performance.

The synthesis of inorganic materials by soft solution processing, which includes precipitation methods, sol–gel process, hydrothermal techniques, allows obtaining fine grained particles and high purity materials at low temperatures in environmentally benign conditions. In precipitation reactions of inorganic materials the addition of organic solvent miscible in water is a routine way to change the ionic strength of the medium to increase the electrostatic interaction between

the ions of opposite charge favouring the formation of insoluble species [6]. In a previous work of the authors [7], it has been studied the preparation of iron(III) phosphate by precipitation from supersaturated aqueous solutions. Different synthesis conditions have been investigated, which give rise to final iron phosphates with different thermal behaviour.

In the present paper we report on the synthesis of iron(III) phosphate by homogeneous precipitation from  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $(\text{NH}_4)\text{H}_2\text{PO}_4$  aqueous, water–ethanol and water–*iso*-propanol solutions at  $\text{pH} = 2.0$  and ambient temperature using hydrogen peroxide as precipitating agent. The precipitates have been characterised by thermoanalytical techniques, chemical analysis, X-ray powder diffraction (XRD) analysis and SEM technique.

## 2. Experimental

### 2.1. Instrumentation

A TG–DTA apparatus SDT 2960 (TA Instruments, Dorking, England) was used. Samples between 5 and 10 mg were heated over the temperature range from ambient to  $800^\circ\text{C}$  at a heating rate of  $10^\circ\text{C min}^{-1}$  in air at a flow rate of  $100\text{ ml min}^{-1}$ .  $\alpha\text{-Al}_2\text{O}_3$  was used as reference material. Samples were run in open platinum pans.

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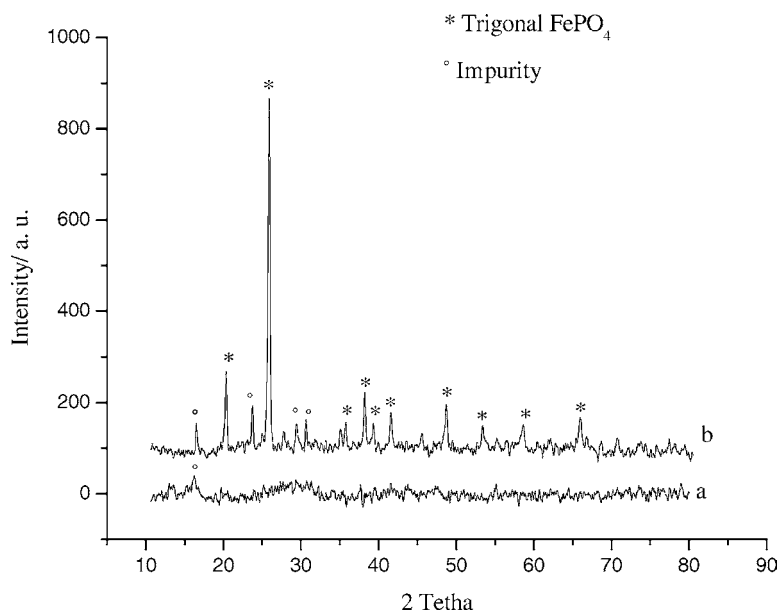


Fig. 1. XRD patterns of the as-precipitate iron phosphate sample obtained from water–ethanol solution at pH = 2.0 and ambient temperature using hydrogen peroxide as precipitating agent (a) and the same sample calcined at 750 °C/10 h in air (b).

pH was measured with a SA520 pH-meter (Orion, Beverly, MA, USA), using a C2005-8 red rod combined pH electrode (Radiometer, Copenhagen, Denmark). For calibration, standard buffer solutions from Aldrich were used.

The elemental composition of the precipitates (Fe, P) was determined by flame and graphite atomic absorption spectrometry (Varian 220 FS, Melgrave Victoria, Australia), after dissolution of the powders in dilute hydrochloric acid.

The precipitates and the calcined products (in air at 750 °C for 10 h) were characterised by X-ray powder diffraction analysis (Philips PW 3710 diffractometer) using Cu K $\alpha$  radiation.

## 2.2. Reagents and standard solutions

Ultra-high-purity water (18 M $\Omega$  cm) obtained from a Milli-Q water production system (Millipore, Bedford, MA) and filtered through a 0.22  $\mu$ m membrane filter was used to prepare all solutions and dilutions. Fe (NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and (NH<sub>4</sub>)<sub>2</sub>H<sub>2</sub>PO<sub>4</sub> (Reagent Grade, Carlo Erba, Italy) crystalline solids were dissolved in de-ionised water to prepare iron and phosphate stock solutions and standardised by atomic absorption spectrometry. Stock solutions were always prepared just before each experiment. Stock standard solutions of iron and phosphorus (Aldrich) at 1000 ppm

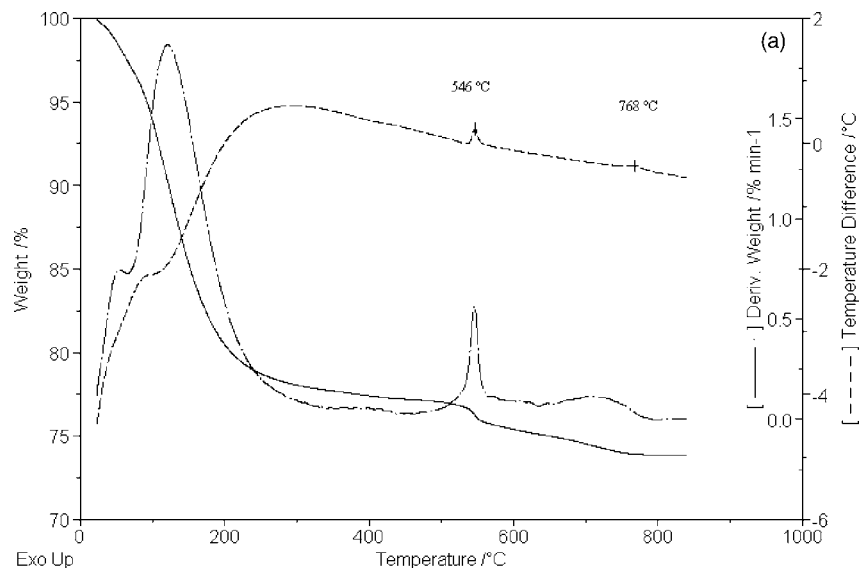


Fig. 2. TG/DTG/DTA curves of the as-precipitate iron phosphate powders obtained from: (a) aqueous solution; (b) water–ethanol solution; and (c) water–*iso*-propanol solution. Heating rate of 10 °C min<sup>-1</sup> in air.

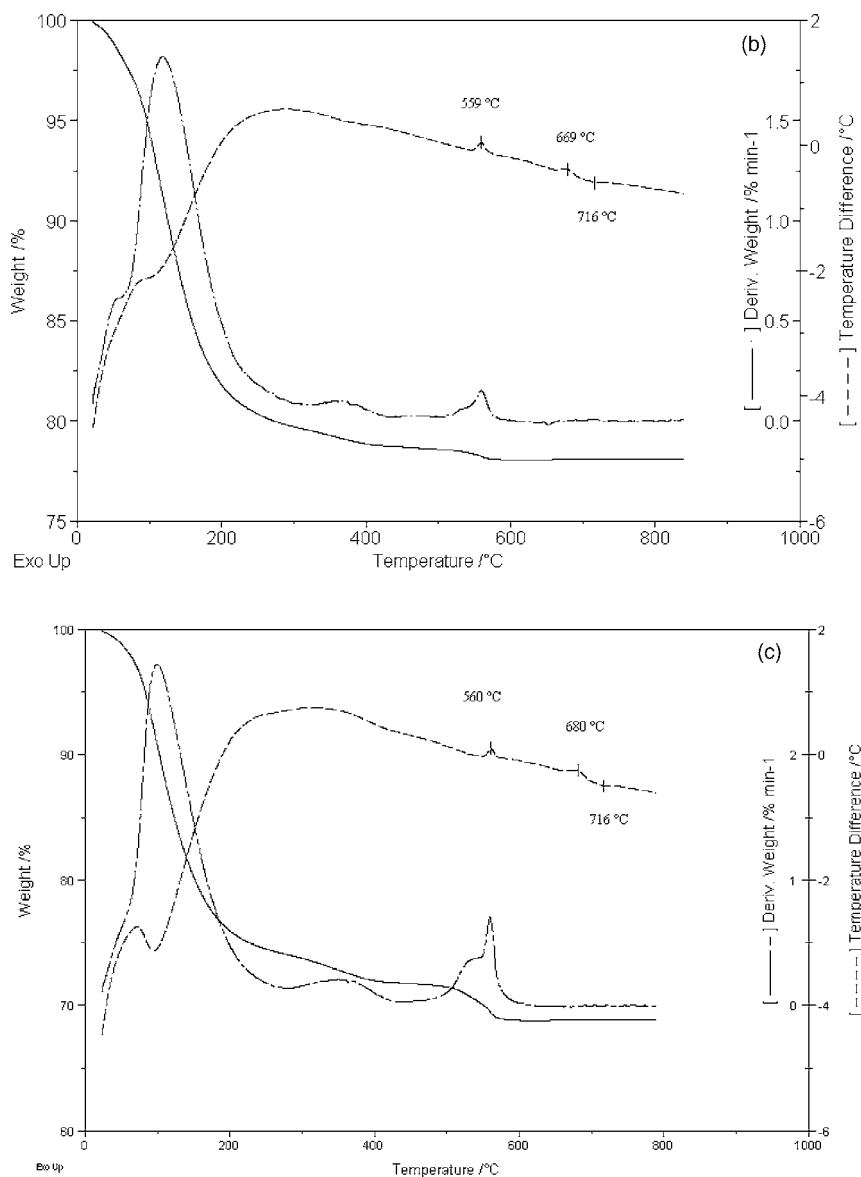


Fig. 2. (Continued).

were used for the preparation of the working standard solutions for the iron and phosphorus AAS determination. All acids used were of analytical reagent grade. Hydrogen peroxide 30% weight (Reagent grade, Ashland Chemical Italiana), ethanol and *iso*-propanol (Reagent Grade, Carlo Erba) were used.

### 2.3. Preparation

A 0.1 M  $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$  solution (having an initial pH of 4.9) was added at ambient temperature to a constantly stirred solution of 0.1 M  $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ , previously dissolved in de-ionised water, water–ethanol (1.5:1, v/v), and water–*iso*-propanol (1.5:1, v/v) solutions, in a 1:1 volume proportion. Three millilitres of concentrated hydrogen peroxide solution were added. Instantly, a white gel-like precipitate

started to form. The precipitates were kept in contact with the mother liquor for 30 min without stirring. The precipitates collected on membrane filter (0.8  $\mu\text{m}$ ) were washed several times with de-ionised water to make the powder free from undesired water-soluble impurity species. The recovered precipitates were dried at room temperature and atmosphere for 2 days. The yield of precipitates was near the theoretical value.

### 3. Results and discussion

All the as-precipitate iron phosphate samples have been identified as being amorphous by X-ray analysis. A poorly crystalline pattern showing only one low angle reflection around  $16.2^\circ$  has been observed for the as-precipitate

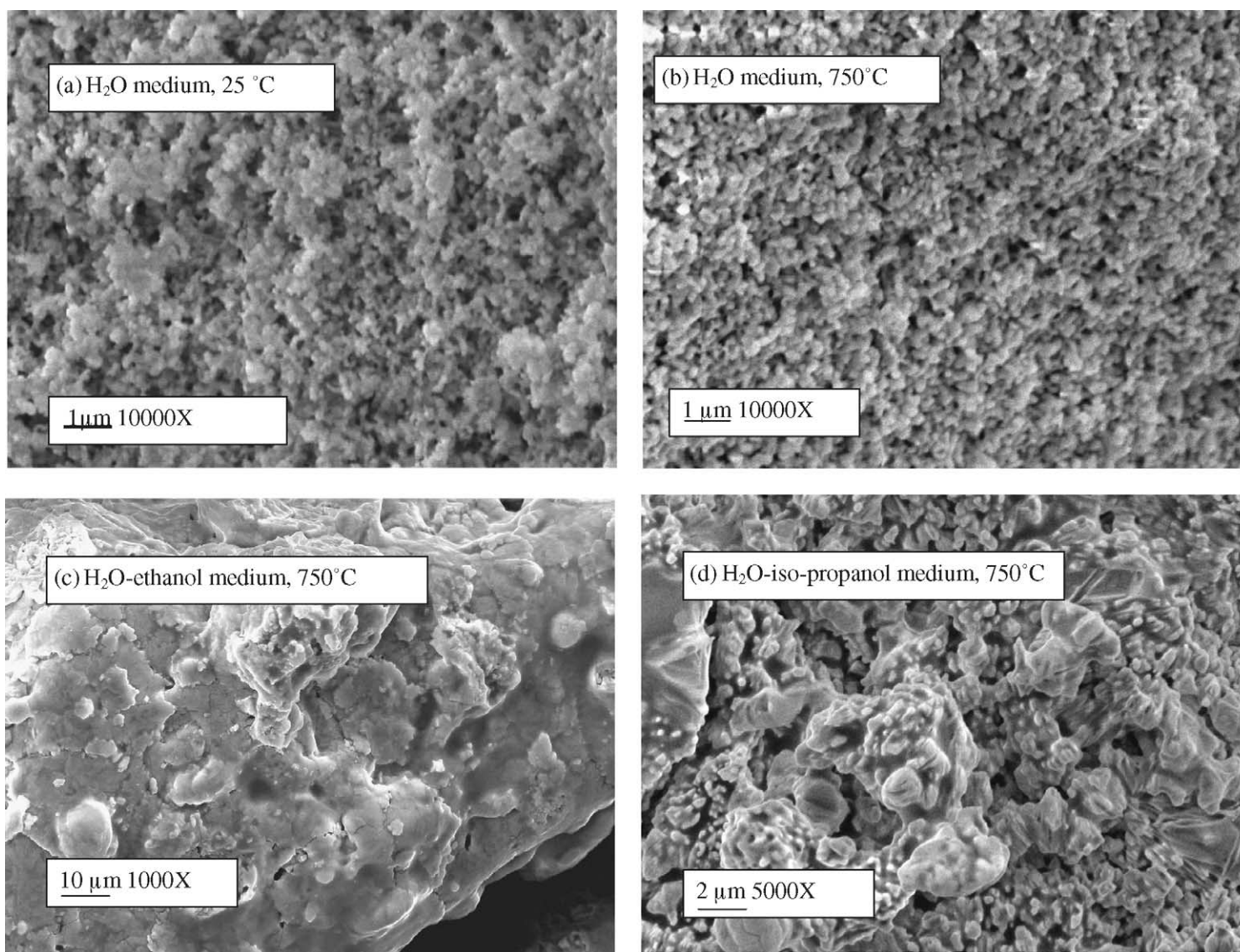


Fig. 3. SEM micrographs of the as-precipitate iron phosphate powders obtained from: (a) aqueous solutions at ambient temperature and (b) the same sample calcined at 750 °C/10 h in air; (c) water-ethanol solution; and (d) water-*iso*-propanol solution and calcined at 750 °C/10 h in air.

samples derived from water-alcohol solutions at ambient temperature. The XRD patterns of the amorphous precipitates calcined at 750 °C/10 h in air showed that the samples are crystalline. The major reflections are attributed to the trigonal quartz-like structure FePO<sub>4</sub> [8], whereas other extraneous minor reflections around 16.2, 27.7, 29.3, and 30.4° are indicative of the formation of Fe<sub>4</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> secondary phase [9]. Exception is made for the calcined precipitate obtained by precipitation from water solution for which all reflections are attributed to the anhydrous iron phosphate [7]. By way of example only XRD patterns of the as-precipitate derived from water-ethanol solution and the same sample calcined at 750 °C are displayed in Fig. 1.

The TG/DTG/DTA curves of the as-precipitate iron phosphate obtained from aqueous solution is shown in Fig. 2a. The TG curve shows a well-defined weight loss between 50 and 500 °C (DTG peak at 120 °C), which is ascribed to elimination of crystallisation water. The total mass loss is 22.0%, which based on the total moles of iron and phosphorus (0.550) in the precipitate, corresponds to 2 moles of H<sub>2</sub>O. The corresponding DTA curve shows one endothermic peak at 115 °C. At higher temperatures a sudden small weight loss of about 1.0% between 500 and 600 °C occurs, which is immediately followed by another small weight loss of about 2.0% as seen in the TG curve. These weight losses were previously [6] associated to co-precipitation of ferric sulphate or ammonium iron alum. The exothermic peak at 546 °C is displayed in the DTA curve. This event was assigned to a transition phase from amorphous to crystalline as evidenced by XRD [10]. Finally, a weak exothermic peak at 768 °C without appreciable weight loss was observed.

The TG/DTG/DTA curves of the as-precipitate iron phosphate obtained from water-ethanol solution is shown in Fig. 2b. The TG curve shows that the elimination of crystallisation water occurs between 50 and 500 °C in two overlapped steps with DTG peaks at 117 and 365 °C. The total mass loss is 20.0%, which based on the total moles of iron and phosphorus (0.540) in the precipitate corresponds to 2 mol of H<sub>2</sub>O. The corresponding DTA curve shows one endothermic peak at 105 °C. At higher temperatures, a sudden small weight loss of 0.5% between 500 and 600 °C was observed. A large exothermic peak at 559 °C was displayed on DTA curve. Again, this event was assigned to a transition phase from amorphous to crystalline form. Further, a small exothermic effect at 669 °C followed by a weak endothermic effect at 716 °C without appreciable weight loss was seen in the DTA curve. The latter effect may be ascribed to the α → β transition as reported for quartz-like materials of type MXO<sub>4</sub> (M = B, Al, Ga, Fe, Mn and X = P, AS) [11].

The TG/DTG/DTA curves of the as-precipitate iron phosphate obtained from water-*iso*-propanol solution is shown in Fig. 2c. The TG curve shows that the displacement of crystallisation water occurs between 50 and 500 °C in two overlapped steps with DTG peaks at 98 and 365 °C. The to-

tal mass loss is 28.0%, which is higher than the expected value for two moles of crystallisation water. Physically adsorbed *iso*-propanol on the surface of the as-precipitate powder could take account for this. The corresponding DTA curve shows one endothermic peak at 105 °C. At higher temperatures a sudden small weight loss of 3.0% between 500 and 600 °C was observed. A large exothermic peak at 560 °C was displayed on the DTA curve. Again this event was assigned to a transition phase from amorphous to crystalline form. Further, a small exothermic effect at 669 °C followed by a weak endothermic effect at 716 °C without appreciable weight loss was observed in the DTA curve. The latter effect may be ascribed to the α → β transition as above-mentioned for the as precipitate derived from water-ethanol solution.

The scanning electron micrographs of the as-precipitate iron phosphate powders showed similar uniform morphological features. The powders consisted of round particles near 80 nm in size along with a narrow size distribution. By way of example only the SEM image of iron phosphate derived from aqueous solution is depicted in Fig. 3a. Conversely, morphological variations with temperature were observed for all the samples. The morphological image of the 750 °C-calcined iron phosphate derived from aqueous medium showed a slightly increase of grain size (crystallites of 200 nm) (Fig. 3b). The SEM micrographs of the 750 °C-calcined FePO<sub>4</sub> derived from alcoholic media showed that crystallites larger than 10 μm in size are yielded, indicating that a sintering process occurs at high temperatures (Fig. 3c and d).

#### 4. Conclusions

Amorphous iron(III) phosphate has been synthesised by homogeneous precipitation from equimolecular Fe(NH<sub>4</sub>)<sub>2</sub>(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> aqueous, water-ethanol and water-*iso*-propanol solutions at pH = 2.0 and ambient temperature using hydrogen peroxide as precipitating agent. The presence of ethanol and *iso*-propanol in the precipitation medium suppressed the co-precipitation of ferric sulphate/or ammonium iron alum as it does in aqueous medium, but trace level of a new secondary phase, Fe<sub>2</sub>(P<sub>2</sub>O<sub>7</sub>)<sub>3</sub> is formed. Thermal treatment at 750 °C yields a crystalline quartz-like structured FePO<sub>4</sub> with markedly different morphological features.

#### References

- [1] M. Ai, K. Ohdam, *Appl. Catal. A* 180 (1999) 47.
- [2] E. Perri, D. Tsamouras, E. Dalas, *J. Cryst. Growth* 213 (2000) 93.
- [3] N. Aliouane, Y. Gagou, E. Elkaim, et al., *Ferroelectrics* 269 (2002) 1127.
- [4] C. Masquelier, P. Reale, C. Wurm, M. Morcrette, L. Dupont, D. Larcher, *J. Electrochem. Soc.* 149 (2002) A1037.

- [5] Y.-S. Hong, Y.J. Park, K.S. Ryu, S.H. Chang, *Solid State Ionics* 156 (2003) 27.
- [6] C.M. Pina, L. Fernandez-Diaz, M. Prieto, S. Veintemillas-Verdaguer, *J. Cryst. Growth* 222 (2001) 317.
- [7] S. Scaccia, M. Carewska, A. Di Bartolomeo, P.P. Prosini, *Termochim. Acta* 383 (2002) 145.
- [8] Natl. Bur. Stand (US) Monogr. 25,16,38 (1979), JCPDS 29-0715.
- [9] Natl. Bur. Stand (US) Monogr. 25,16,38 (1979), JCPDS 36-0318.
- [10] P.P. Prosini, M. Lisi, S. Scaccia, M. Carewska, F. Cardellini, M. Pasquali, *J. Electrochem. Soc.* 149 (2002) A297.
- [11] E. Philippot, A. Goiffon, A. Ibanez, M. Pintard, *J. Solid State Chem.* 110 (1994) 356.