Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 997–1007

USE OF EMANATION THERMAL ANALYSIS IN CHARACTERISATION OF NANOSIZED HEMATITE PREPARED BY DRY GRINDING OF GOETHITE

L. A. Pérez-Maqueda[1]*, J. Šubrt*[2]*, V. Balek*[3*]*, J. M. Criado*[1] *and C. Real*[1]

[1]Institute of Materials Sciences, C.S.I.C., Seville University, c-Americo Vespucio s/a
Isla de La Cartuja, 41092 Sevilla, Spain
[2]Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, CZ-250 68 Řež
[3]Nuclear Research Institute, CZ-250 68 Řež, Czech Republic

Abstract

Hematite nanoparticles of narrow size distribution were prepared by grinding of goethite. Intermediate and final products of grinding were characterised by different techniques, including the less-common emanation thermal analysis (ETA). ETA was shown to be a useful technique for characterising processes of surface annealing, initial sintering and growth of hematite particles under in situ conditions of thermal treatment. A good agreement was found between results of ETA, TG, XRD, IR spectrometry, transmission electron microscopy and scanning electron microscopy, used for characterisation of thermal behaviour of the goethite samples ground for varying time (0–70 h).

Keywords: emanation thermal analysis (ETA), goethite, grinding, mechanochemical decomposition, nanosized hematite particles

Introduction

A large number of applications of hematite (α-Fe_2O_3), including its use as precursor for maghemite synthesis, were recently described [1]. Different methods for the preparation of hematite with controlled morphology and particle size were reported in the literature [2–5]. The use of goethite (α-FeOOH) as precursor for the synthesis of hematite is based on the experimental observations that goethite undergoes a topotactic transformation into hematite on heating [6] and that goethite and other oxide hydroxides decompose to hematite by mechanical treatment [7–14]. Nevertheless, there is a lack of information on the morphology and texture of the intermediate and final products of the mechanical treatment.

A less-common method, emanation thermal analysis (ETA), was used in this paper for studying the textural and structural changes in solids during thermal and/or mechanical treatment. It was demonstrated earlier [15–18] that ETA makes it possible to obtain information about changes in surface area, microporosity, particle

---

[*] Author for correspondence: E-mail: bal@nri.cz

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

growth, and formation of new phases taking place during sample heating or cooling. Fine and hyperfine changes in the solids and their surfaces, which cannot be detected by TG and DTA, were indicated by changes of radon release rate measured under in situ conditions of thermal treatment. In our previous paper [16], ETA was successfully used for characterisation of the influence of grinding on the textural and structural properties of nanosized titania powders. Therefore, ETA was used in this study for characterisation of the microstructure of goethite and its grinding products when heated from 20 to 1200°C in air. The results of ETA and other complementary techniques are compared, with the aim of obtaining additional information about the micrstructure changes and growth of the grains of ground goethite samples.

Experimental

Materials and preparation of samples

A goethite (α-FeOOH) sample, denoted B 940 (Bayer AG, Germany), was used as feed material. A non-ground goethite sample and samples ground for 18 and 70 h, were investigated.

A planetary mill (Pulverisette 5, Fritsch, Germany), with a speed of 660 r.p.m. was used for mechanical treatment of the goethite. The mill was equipped with two agate jars of 50 ml containing 7 agate bowls of 12 nm diameter each. Approximately 15 g of goethite were placed into each jar and the grinding was interrupted after 18 and 70 h, to collect 0.3 g of the intermediate products for their characterisation. The temperature of samples was monitored during grinding, making it possible to interrupt the grinding when the temperature increased above room temperature.

Methods used for sample characterisation

Taking into account that ETA is a less-common method, we shall describe its principles to the extent that is necessary for the discussion and interpretation of the results.

ETA [17, 18] involves the measurement of the rate of radon release from samples previously labelled. Atoms of radon, ^{220}Rn, were formed by the spontaneous alpha decay of ^{228}Th and ^{224}Ra. The ^{224}Ra and ^{220}Rn atoms were incorporated into the sample to a maximum depth of 100 nm due to the recoil energy (85 keV/atom) which the atoms gained by the α- spontaneous decay.

A part of the radon atoms formed by spontaneous α-decay of radium is directly released from the sample by recoil. Another part of the radon atoms is trapped in the lattice defects, such as vacancy clusters, grain boundaries and pores, and can be released from the sample by diffusion. The defects in the solids serve both as traps and diffusion paths for radon. The radon release rate depends on the surface area and on the radon diffusion parameters in the solid [18].

The mechanisms of radon release from powder samples are (i) release due to the recoil energy of the radon atoms, (ii) diffusion in open pores and in intergranular space, and (iii) radon diffusion in the matrix of the solids. The radon release rate, E (also called emanating rate), can be written:

$$E=E(\mathrm{recoil})+E(\mathrm{pores})+E(\mathrm{matrix}) \tag{1}$$

The emanating rate due to recoil can be expressed as:

$$E(\mathrm{recoil})=K_1S_1 \tag{2}$$

where K_1 is a temperature independent constant, proportional to the penetration depth of the recoiled radon atoms in the solids investigated, and S_1 is the external geometrical surface area of the sample particles.

The term E(pores) of the emanating rate which is due to radon diffusion in the intergranular space and open pores can be expressed as:

$$E(\mathrm{pores})=K_2S_2 \tag{3}$$

where K_2 is a constant that depends on temperature, and S_2 is the internal surface area of the sample and depends on the surface of the open pores and intergranular voids.

E(matrix), attributable to radon diffusion in the solid matrix of the sample, can be expressed as:

$$E(\mathrm{matrix})=K_3\exp(Q/2RT)\ S_3 \tag{4}$$

where K_3 is a constant comprising the atomic properties of the lattice, Q is the activation energy of Rn diffusion in the solid matrix, S_3 is the surface area representing the sum of the cross-section of all diffusion paths with the surface (dislocations, grain boundaries, etc.), R is the gas constant, and T the temperature on the absolute scale.

Consequently, processes that can be investigated by means of ETA are those accompanied by changes of surface area and/or microstructure of the solid samples, affecting the diffusion release of inert gas from the solids. For low temperatures, where no thermal diffusion of radon in the matrix is assumed, the values of E are proportional to the surface area. For temperatures where radon diffusion in the matrix takes place, such a direct relationship cannot be assumed. A decrease in E corresponds to a densification of the structure, closing of pores and/or a decrease in the surface area of the sample.

The ETA–DTA measurements were carried out at the Nuclear Research Institute, Ře using modified NETZSCH DTA 404 equipment. A heating rate of 5, a cooling rate of 2.5 K min^{-1}, and an air flow of 50 ml min^{-1} were used. During the ETA measurements, a labelled sample of 0.05 g was situated in a corundum crucible immersed in a constant air flow, which carried the radon released from the sample into a chamber for measuring the radon radioactivity [17]. For ETA measurements, samples were labelled using the adsorption of traces of ^{228}Th and ^{224}Ra on the sample surface from acetone solution. The specific activity of a sample was 10^5 Bq per mL. Samples were stored for three weeks prior to ETA measurements to allow radioactive equilibrium to be reached.

Thermogravimetric measurements were carried out using a Stanton Redcroft model TG770. A sample mass of 0.03 g was placed in an alumina crucible. A heating rate of 5 K min^{-1} and an air flow of 50 ml min^{-1} were used.

Transmission electron microscopic (TEM) examinations were performed with a Philips CM 10 microscope. The samples were first ultrasonically dispersed in ethanol; a drop of this dispersion was then deposited on a thin carbon film supported by a copper grid.The X-ray diffraction (XRD) patterns were obtained with CuK$_\alpha$ radiation (Model PW 1060, Philips). The dimensions of the coherently diffracting domains (crystallite size) of hematite were determined from the full-width of the half maximum of the (104) and (110) XRD peaks using Scherrer's equation.

The IR spectra of the samples were measured in TlBr pellets (Pye-Unicam PU 9512 spectrometer). A concentration of 1 mg of the sample in 300 mg TlBr was used for all measurements.

The surface area measurements were carried using the single point B.E.T. method (Micromeritics 2000 apparatus). The equivalent spherical particle diameter (d_{VA}) can be calculated from the surface area with the following expression:

$$d_{\mathrm{VA}}=\frac{6}{\sigma S} \tag{5}$$

where d_{VA} is the particle diameter (μm), σ density (g cm^{-3}) and S is the surface area (m^2 g^{-1}), determined by B.E.T. The equivalent spherical particle diameter is defined as the diameter of a sphere with the average surface area of the particles of the solid sample, whatever their shape is.

Results and discussion

Figure 1 presents the TEM micrographs of a goethite non-ground sample and of samples ground for 18 and 70 h. The initial goethite sample contained aggregated acicular sub-units. (Fig. 1a). The sample ground for 18 h contained aggregates of round particles approximately 15 nm in diameter (Fig. 1b). As observed in Fig. 1c, the particle size of the goethite sample ground for 70 h was significantly larger.

Figure 2 shows the XRD patterns of initial goethite samples ground for 18 and 70 h. The XRD pattern of the non-ground sample is characteristic of crystalline goethite.

For the sample ground for 18 h, the diffraction peaks of goethite were broadened, indicating that the amorphization of initial goethite took place during grinding. The presence of a small amount of hematite phase was detected in the sample ground for 18 h.

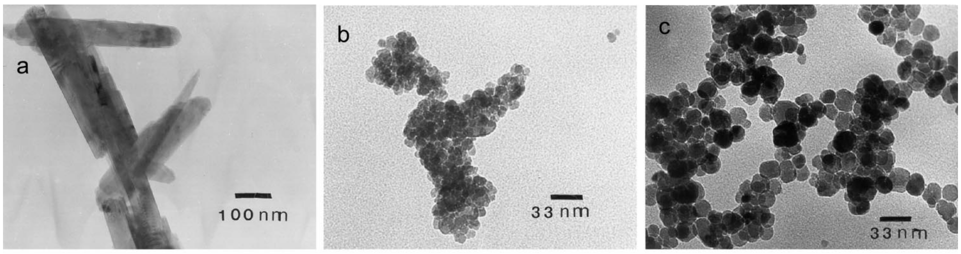

Fig. 1 Transmission electron micrographs of goethite before heating: (a) non-ground sample, (b) sample ground for 18 h, and (c) sample ground for 70 h

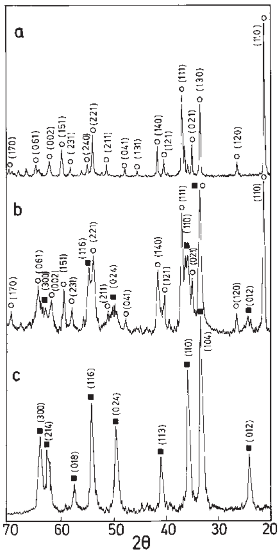

Fig. 2 X-ray diffraction patterns for the a – non-ground goethite sample, b – goethite sample after 18 h grinding and c – goethite sample after 70 h grinding. Peaks notation: o – goethite; ■ – hematite

The XRD pattern of the sample ground for 70 h is characteristic of pure hematite. No intermediate products were observed by XRD.

Figure 3 demonstrates the characteristic IR spectra in the range 500–1100 cm^{-1} for the three investigated samples of B940 goethite, namely the original, non-ground goethite and samples ground for 18 and 70 h. The two bending vibration bands for the original sample at 800 (δ-OH) and 897 cm^{-1} (γ-OH) are characteristic of goethite. Because of the decrease in crystallinity after grinding goethite for 18 h, these two bands exhibited a decrease in frequencies, shifting to 792 and 882 cm^{-1}, and broadening. For the sample ground for 70 h, the mentioned vibration bands were not detected, which confirmed, that total goethite→hematite conversion took place. The results of IR spectroscopy were in agreement with the conclusions reported on the basis of XRD patterns.

Thermogravimetry results (Fig. 4 for TG and DTG curves) of the original goethite (curve a) indicated that thermal decomposition of the samples took place in three steps. We have assumed that in the temperature range from 40 to 170°C the release of water molecules from the sample took place, and that the sample mass decrease in the temperature ranges from 170 to 300 and 300–370°C corresponded to the dehydroxylation of goethite. The sample ground for 18 h was partially dehydrated. Consequently, the TG results (Fig. 4, curve b) reflected this effect of grinding. Nevertheless, the dehydroxylation took place in the same temperature range as observed with the non-ground sample.

On the TG results of the sample ground for 70 h (Fig. 4, curve c), the small mass loss in the range from 200 to 700°C can be attributed to the release of lattice water, as

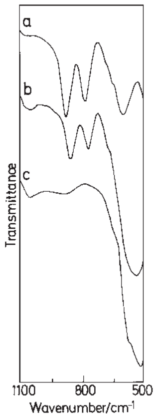

Fig. 3 IR spectra of a – non-ground goethite sample, b – goethite sample after 18 h grinding, and c – goethite sample after 70 h grinding

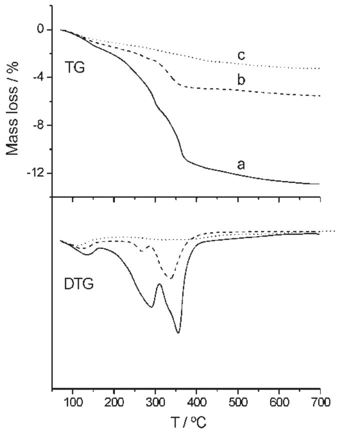

Fig. 4 TG and DTG curves of a – non-ground goethite sample, b – goethite sample after 18 h grinding and c – goethite sample after 70 h grinding. Heating in air flow at a rate of 5 K min^{-1}

described by Wolska [21]. As confirmed by XRD and IR, the sample ground for 70 h was totally transformed into hematite (Figs 2 and 3).

Particle-size diameters calculated from the TEM micrographs (Fig. 1) for the goethite samples after different grinding times are presented in Table 1, together with values of the surface area of the original and ground samples. Equivalent spherical particle diameters were calculated from the surface-area values of ground samples. Good agreement between values of the particle diameter calculated from surface-area and from TEM micrographs was found. The decrease in particle-size values calculated for the samples ground for 18 and 70 h, can be interpreted by assuming that the particles are non-porous and do not undergo cold-welding during the grinding process.

From the XRD patterns, especially the calculated full-with of the half maximum (FWHM) of the (104) and (110) diffraction peaks, it followed that the sample ground for 70 h contains hematite of a crystallite size of ~12 nm in both directions. This value is very similar to that estimated from the TEM micrographs, indicating that hematite particles consisted of rounded nanosized single crystals.

Table 1 Changes caused by grinding in synthetic goethite

Grinding time/h	BET surface area/ $m^2 g^{-1}$	Equivalent spherical particle diameter calculated from BET/ nm	TEM particle size/nm
0 (non-ground)	10	113	–
18	81	14	14±9
70	73	16	15±5

The ETA results (Fig. 5) are presented as the temperature dependences of the radon release rate, *E*, normalised to the total radioactivity of the parent nuclides adsorbed on the sample. It is known that bulk diffusion in an inorganic solid does not start below the Tamman temperature, which is close to half of the absolute melting temperature of the solid [22]. Thus, the radon release rate from hematite samples at temperatures lower than 780°C is due to recoil and radon release from external geometrical surfaces, intergranular space and open pores as described by Eqs (2) and (3). Therefore, the ETA results measured at temperatures lower than 780°C reflect changes in sample surface and opened porosity. On the other hand, for temperatures above the Tamman temperature, the radon release is due to diffusion in the bulk. The interpretation of the ETA curves will be discussed in comparison with results of thermogravimetry, XRD, and SEM.

As indicated by the TG and DTG curves in Fig. 4, the release of adsorbed water from the non-ground goethite sample took place at temperatures lower that 170°C.

An increase of the radon release rate was observed on heating the sample in the temperature range 40–170°C, when water was removed from the sample.

As observed by ETA (curve a, Fig. 5), this process was accompanied by an increase of *E* in the same temperature range. For the interpretation of the ETA results, it

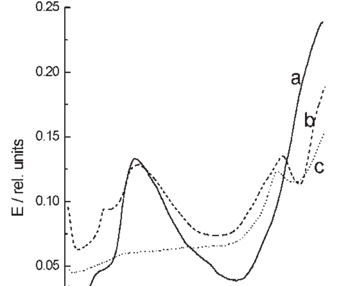

Fig. 5 ETA results of a – non-ground goethite sample, b – goethite sample after 18 h grinding and c – goethite sample after 70 h grinding. Heating in air flow at a rate of 5 K min^{-1}

should be mentioned that the removal of water molecules from the sample opened new diffusion pathways for radon released from the sample grains. A decrerase of *E* in the temperature range 170–230°C was observed.

The important increase in the radon release rate, *E*, in the temperature range 230 to 290°C corresponds to radon release in open pores and intergranular interstices during the thermal dehydroxylation of goethite. It is well known (e.g. [23]) that a porous product results during dehydroxylation of goethite. The dehydroxylation was therefore characterised by the increase in the release rate of ^{220}Rn.

As expected, the observed increase of *E* was more remarkable for the non-ground sample (Fig. 5, curve a) than for the sample ground for 18 h (curve b), which had been partially transformed into hematite by grinding. No effect was observed on the ETA curves in this temperature range, for the sample ground for 70 h (curve c), which had been completely converted to hematite. The TG and DTG results agree with this interpretation.

The decrease of the radon release rate, *E*, observed at temperatures ranging from 290 to 800°C in curve a, Fig. 5, indicated the annealing of porosity formed during the previous dehydroxylation of goethite.

Interesting information was obtained by ETA for ground goethite samples (curves b, c in Fig. 5). The increase of the radon release rate, *E*, due to radon diffusion, starting at about 800°C was interrupted by a remarkable decrease of *E* in the temperature range 950–1070°C, which can be ascribed to the initial sintering of hematite particles. XRD patterns (Fig. 2) already demonstrated that the mechanical treatment of goethite caused amorphisation of the sample, giving rise to structure defects and enhancing sintering of ground particles. This effect was observed by the decrease of *E* starting at approximately 950°C on the ETA curves of ground samples.

The increase of *E*, observed on heating above 1070°C, indicated that, at this temperature, the radon diffusion along grain boundaries and remaining pores prevailed over the surface decrease accompanying initial sintering of hematite particles. Grain boundaries and pores, serving at the low-temperature range as traps for radon atoms (atom size 0.38 nm), served in the temperature range above 1070°C as diffusion paths for radon. Thus, the enhanced increase of radon release rate characterised the process of migration of grain boundaries towards the surface of samples. Grain boundary diffusion has been considered as the mechanism for growth of hematite grains involved in the sample.

Quite different thermal behaviour was observed for the non-ground sample in this temperature range. As it follows from the ETA results (Fig. 5, curve a), a smooth exponential-like temperature dependence of radon release rate *E* was observed in the temperature range from approximately 800 to 1050°C. Nevertheless, a slowing of the radon release rate was observed on heating the sample in the temperature range 1050–1200°C. The onset of initial sintering of the hematite particles resulting from dehydration of non-ground goethite can be assumed to occur at this temperature. This interpretation was supported by SEM micrographs (Figs 6 and 7).

The ETA curves should be considered as superimpositions of temperature dependences of radon release rate due to several mechanisms controlling the rate of radon release from the sample, namely recoil, diffusion in pores, and diffusion of radon in the matrix (Eqs (1)–(4)). The mathematical treatment of the ETA results will be published in our next paper.

From ETA results in Fig. 5, it follows that values of the emanating rate, E_{780}, measured at 780°C for the non-ground sample and the ground samples differ. The E_{780} values for the ground samples were considerably higher than the E_{780} value for the non-ground sample. Obviously, the partially amorphised goethite, formed during 18 h grinding, yielded after heating to 780°C a product of larger surface-area, containing higher structural disorder than non-ground crystalline goethite. The differences in the E_{780} values for 18 and 70 h ground samples, reflected the different history (grinding time) of the sample.

The ETA curves measured in the temperature range 780–1200°C (Fig. 5, curves b, c) revealed the following differences between the samples ground for 18 and 70 h: the onset of the initial sintering indicated on the curve c (70 h grinding) was observed at a temperature 25°C lower than observed on curve b (18 h grinding time). The subsequent decrease of E characterised the kinetics of initial sintering during the non-isothermal heating conditions: the decreasing slope was lower for the sample ground for 70 h (curve c) compared with the sample ground for 18 h (curve b). A higher rate of increase of radon release was observed in the temperature range 1100–1200°C than was found for the sample ground for 18 h compared with the sample ground for 70 h.

This interpretation agreed well with the SEM micrographs for the non-ground and ground goethite samples heated to 708 and 1209°C, respectively, (Figs 6 and 7, respectively), i.e. to the temperatures just before the enhanced radon diffusion started, and to the upper temperature limit of the ETA measurements. No changes

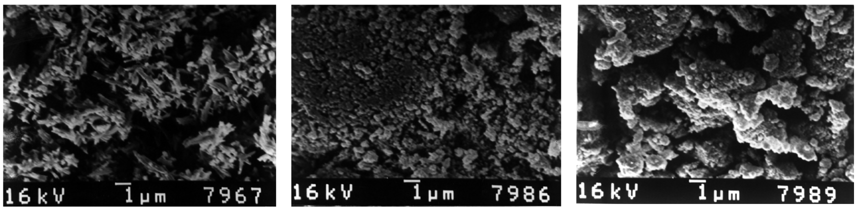

Fig. 6 Scanning electron micrographs of hematite samples heated to 708°C originating from a – non-ground goethite sample, b – goethite sample ground for 18 h and c – goethite sample ground for 70 h

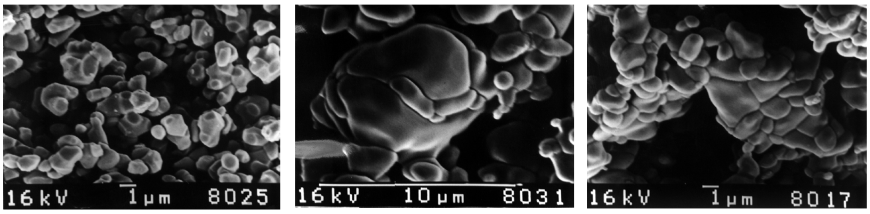

Fig. 7 Scanning electron micrographs of hematite samples heated to 1209°C originating from a – non-ground goethite sample, b – goethite sample ground for 18 h and c – goethite sample ground for 70 h

were observed on DTA and TG curves measured in this high temperature range. Using the SEM micrographs in Figs 6 and 7, the respective non-ground and ground samples heated to 708°C can be characterised as follows:

Samples heated to 708°C

The non-ground sample preserved its characteristic acicular character, the maximum length of the particles being 1 μm, and thickness 0.1 μm. The sample ground for 18 h consisted of agglomerates approximately 0.1–0.8 μm in size. The sample ground for 70 h consisted of agglomerates of comparable size.

Samples heated to 1209°C

In the non-ground sample, sintered grains 0.7–2.0 μm in size were observed. In the sample ground for 18 h, sintered grains of 2–5 μm in size were observed. With this sample the most intense grain growth took place. In the sample ground for 70 h sintered grains 0.8–2.0 μm in size were observed. With this sample a slightly lower intensity of grain growth was observed in the mentioned temperature range than with the sample ground for 18 h.

In this way, we have seen that ETA is a sensitive technique for studying the interaction of hematite particles and their further grain-growth on heating. The above results confirmed our previous statement that grinding of samples caused a lowering of the sintering temperature with regard to non-ground material [16].

Conclusions

ETA supplied important additional information about surface annealing, interactions of hematite particles during early sintering of the sample, changes in porosity, and growth of hematite grains characterised under in situ conditions of heating. The ETA results complemented the results of other techniques used in this paper for characterisation of hematite nanosized particles prepared by grinding of goethite.

* * *

A part of the experimental results was obtained in the frame of the research grant PZCH/06/97 provided by Ministry of Industry and Trade of the Czech Republic. The manuscript was prepared in co-operation between Academy of Sciences of the Czech Republic and the C.S.I.C., Spain. The authors are indebted to Mrs. E. Klosová, Nuclear Research Institute, Ře, for ETA measurements.

References

1 R. M. Cornell and U. Schwertmann, The Iron Oxides. Structure, Properties, Reactions, Occurence and Uses, (VCH, Weinhein 1996).
2 M. Moráles, T. González-Carreño and C. Serna, J. Mater. Res., 7 (1992) 2538.
3 E. Matijević and S. Cimas, Colloid Polymer Sci., 265 (1987) 155.
4 R. Sapieszko and E. Matijević, J. Colloid Interface Sci., 74 (1980) 405.

5 M. Cabañas, M. Vallet-Regi and J. González-Calbet, J. Mater. Res., 8 (1993) 2694.

6 L. A. Pérez-Maqueda, J. M. Criado, C. Real, J. Šubrt and J. Bohacek, J. Mater. Chem., in press.

7 J. Rendon, J. Cornejo and P. D. Arambari, J. Colloid Interface Sci., 94 (1983) 546.

8 E. Mendelovici, S. Nadiv and I. Lin, J. Mater. Sci., 19 (1983) 1556.

9 E. Mendelovici, R. Villalba and A. Sagarzu, Mat. Res. Bull., 17 (1982) 241.

10 J. Jiménez-Mateos, J. Moráles and J. Tirado, J. Mat. Sci. Letters, 5 (1986) 1295.

11 D. Klissurski and V. Blaskov, J. Chem. Soc., Chem. Commun., (1983) 863.

12 R. Gómez-Villaciegos, L. Hernán, J. Moráles and J. L. Tirado, Mat. Res. Bull., 22 (1987) 513.

13 R. Gómez-Villacieros, J. Morales and J. Tirado, J. Chem. Soc., Chem. Commun., (1984) 559.

14 J. Šubrt, A. Nosek, V. Procházka and V. Zapletal, J. Chem. Soc., Chem. Commun., (1986) 1713.

15 V. Balek, E. Klosová, M. Murat and N. A. Camargo, Amer. Ceram. Soc. Bull., 75 (1996) 73.

16 C. Real, J. M. Criado and V. Balek, J. Mater. Sci., 33 (1998) 5247.

17 V. Balek, Thermochim. Acta, 192 (1991) 1.

18 V. Balek and J. Tölgyessy, Emanation Thermal Analysis in: Wilson and Wilson's, Comprehensive Analytical Chemistry, Part XII C, Elsevier Sci. Publishers, Amsterdam 1984, p. 304.

19 P. Cambier, Clay Min., 21 (1986) 192.

20 U. Schwertmann, P. Cambier and E. Murad, Clays Clay Min., 33 (1985) 369.

21 E. Wolska, Z. Kristallogr., 154 (1981) 69.

22 N. N.Greenwood, Ionic Crystals, Lattice Defects and Non-stoichiometry, (Butterworths, London 1968).

23 J. Šubrt, V. Balek, J. M. Criado, L. A. Pérez-Maqueda and E. Večerníková, J. Therm. Anal. Cal., 53 (1998) 509.