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A micro-Raman study of iron-titanium oxides obtained by sol-gel synthesis

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Iron-Titanium mixed oxides in powders and thin films on glass substrates have been prepared at different composition by using the sol-gel method. The thermal evolution, revealing the formation of different crystalline phases, has been followed by means of the micro-Raman spectroscopy. Pseudobrookite was the only crystalline phase found involving both iron and titanium. The differences in the thermal behavior between powders and films and the influence of iron as impurity in the crystallization process of the titania were also studied.

1. Introduction

Iron and titanium oxides are extensively studied for many technological applications, being, for example, of huge importance in corrosion studies and in biotechnology, respectively [1–6]. More recently, mixed iron-titanium oxides have been proposed due to their mechanical, optical and electrochemical properties, for example as electrochromic devices or as humidity sensors [7–10]. In addition, hydrous titanium oxide has attracted attention as ion exchanger or for adsorption purposes and its properties may be improved by preparing mixed oxides of titanium with other metal ions.

The sol-gel technique [11, 12] enables one to obtain oxides in a relatively simple way and at low temperatures as bulk, powder or films both in crystalline or amorphous form. The process starts in an alcoholic solution containing metal precursors suitable for polymerization, as alkoxides. Subsequent hydrolysis and policondensation reactions lead to the gel formation. In the gel the local order is on a very short scale: additional heat treatments, by means of the elimination of the organic components, lead to the formation of nanocrystalline aggregates and then powders with larger crystalline size. The composition and the microstructure may be finely controlled and tailored for specific uses in the whole sol-gel process.

Thin films (with thickness ranging from tenths to hundreds of nanometers) are easily obtained through the sol-gel route by the dip coating technique, i.e. by dipping a specific substrate (glass, quartz, silicon) directly in the precursors solution and then obtaining the polimerization and the removal of the organics by means of thermal treatments. A residual presence of organics in the gel may give different morphologies or even induce different crystalline phases [13].

In this work we will investigate by micro-Raman spectroscopy the phase formation, for different preparations and heat treatments, in the production of Fe/Ti mixed oxides, both as powders and thin films, at different Fe : Ti ratios.

2. Experimental

Iron-titanium oxides are here obtained by sol-gel synthesis starting from titanium tetra-isopropoxide (TPOT) and iron nitrate. Two different series of samples have been produced starting from high and low Fe concentrations, respectively.

Samples at high Fe : Ti ratios (Fe : Ti = 0.5 : 1; 1 : 1; 1.5; 1) have been prepared to study the possible mixed phases (pseudobrookite Fe_2TiO_5 and ilmenite $FeTiO_3$) and the phase transformations occurring during the heating processes. In this case both powders and films have been produced.

With a Fe content of only a few percent (2-5–10%), on the other hand, the attention was focused on the effect of Fe as impurity in the crystallization behavior of TiO_2 into its possible phases anatase, rutile and brookite.

The preparation of high Fe concentration iron-titanium oxides has been performed by dissolving TPOT and $Fe(NO_3)_3{\cdot}9H_2O$ in ethanol (0.3 M) and by mixing the solutions in different proportions as to obtain solutions with molar ratios Fe : Ti of 0.5 : 1; 1 : 1; 1.5 : 1. The solutions have been stirred for hours to obtain homogeneous sols. The details of the preparations may be found also in the paper by Macek *et al*. [14].

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The films have been pre-heated in an oven at 50 °C for the evaporation of the ethanol and then heated at 300 °C (first type of samples) and at 500°C (a second type of samples) for two hours. The films have been obtained by a total of nine dip-coatings: the pre-heating has been performed after each dipping and the heating at 300 °C or 500 °C every three depositions. The thickness of the films after three depositions, measured by a step-profiler, was found to be roughly 150 nm.

To prepare the powdered samples, the starting solutions have been left to gelify in air, then heated in an oven up to 300 °C (at a rate of 60°C/hour) or at 500 °C (at a rate of 100°C/hour) and maintained at 300 °C or 500 °C for 40 hours.

The samples at low Fe concentration were obtained by adding different proportions of $Fe(NO_3)_3{\cdot}9H_2O$ to a solution 0.5 M of TMET (titanium tetra-methoxyethoxyde) in methoxy-ethanol. TMET was obtained by a distillation of TPOT in methoxy-ethanol. Molar ratios Fe : Ti equal to 2 : 100, 5 : 100, 10 : 100 were obtained. The solutions were gelified in air and then heat treated up to 1000 °C at a rate of 100°C/hour. Powdered samples have been taken every 100 °C, to have a complete range 100–1000 °C.

The Raman spectra of powders and films at high Fe contents were recorded at RT with an ISA-Labram micro-Raman apparatus using the 632.8 nm line of an He-Ne laser as excitation. The laser power was kept lower than 1 mW on the sample by the insertion of density filters, in order to avoid undesired heating effects. The Raman spectra of the powders with low iron content were recorded with a Dilor XY micro-Raman using the 514.5 nm line of an Argon Laser.

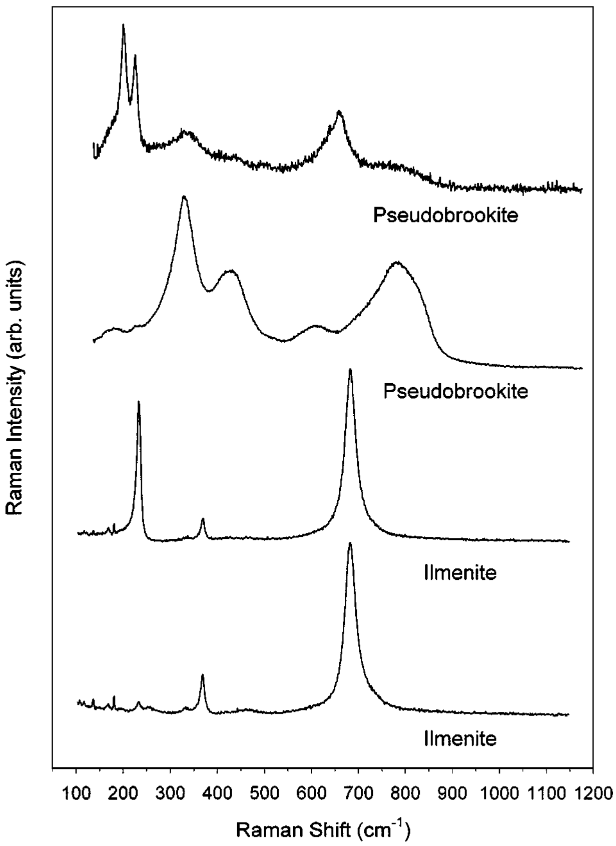

Figure 1 Raman spectra along two different directions for natural crystals of ilmenite and pseudobrookite.

3. Results

3.1. High Fe concentration

At high Fe content (Fe : Ti ratio of 0.5 : 1, 1 : 1, 1.5 : 1) we studied both powders and films. In the films we observe large cracks due to the shrinkage during the thermal treatments: the Raman spectrum is however relatively insensitive to the position on the film. In order to have some reference for the spectra of the most common iron-titanium mixed oxides, we performed the Raman spectra of natural crystals of ilmenite (Parma – Italy) and pseudobrookite (Utah - USA) which are reported in Fig. 1. The spectra depend on the sample orientation and accurate polarization measurements interpreted on the basis of the Raman selection rules will be presented elsewhere.

The Raman spectra of the films at various composition are reported in Fig. 2. The film with Fe : Ti = 0.5:1 at 300 °C shows a Raman spectrum typical of an amorphous system. At 500 °C the spectrum is a superposition of the broadened bands of the anatase [15] and some features assigned to the pseudobrookite phase. Also at Fe : Ti = 1 : 1 at 300 °C we observe an amorphous phase, which crystallise in pseudobrookite at 500 °C. At Fe : Ti = 1.5 : 1 the pseudobrookite is already present at 300 °C and its Raman spectrum becomes better defined at 500 °C. For all compositions the titanium excess is found presumably as an amorphous phase.

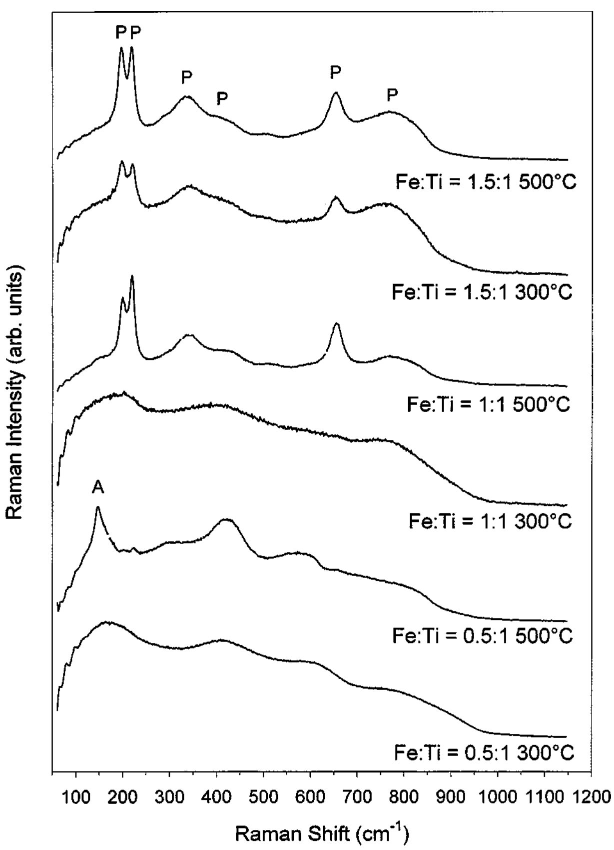

Figure 2 Raman spectra of the Fe/Ti films at different compositions and annealing temperatures (P = Pseudobrookite; A = Anatase).

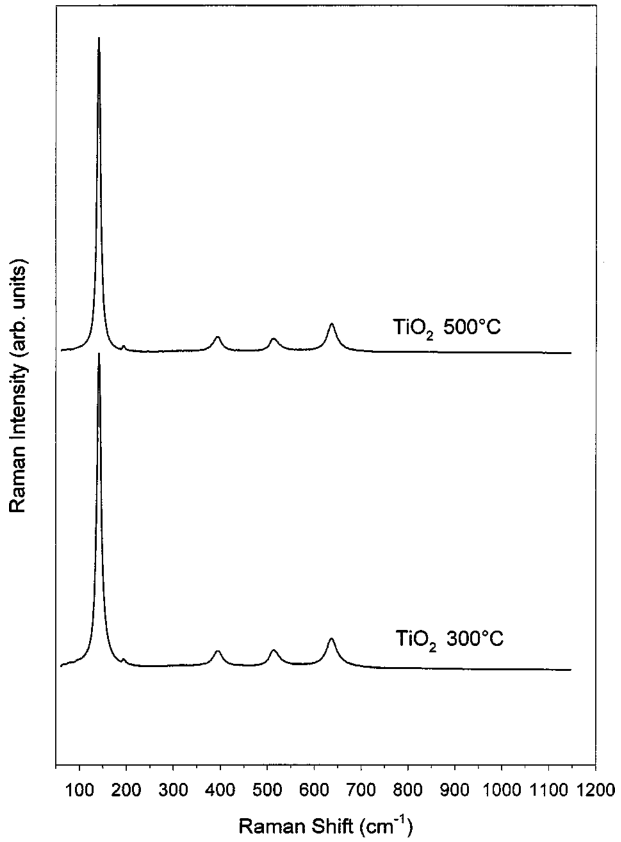

Figure 3 Raman spectra of powders of pure titania TiO_2 annealed at 300°C and 500 °C.

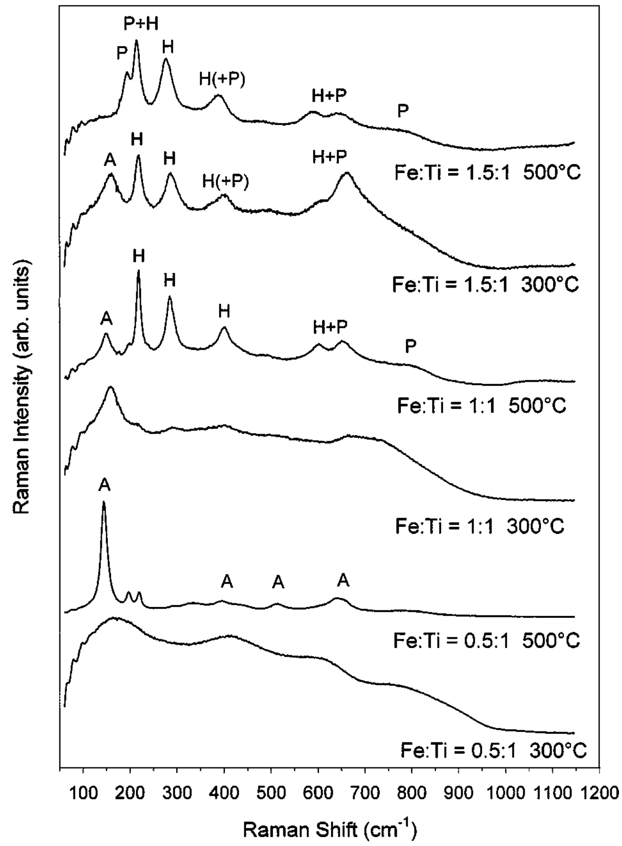

Figure 4 Raman spectra of the Fe/Ti powders Fe/Ti at different compositions and annealing temperatures (P = Pseudobrookite; A = Anatase; H = Hematite).

The powders give different results with respect to the films. The Raman spectra of the powders of pure titania show the expected anatase peak, well defined already at 300 °C (Fig. 3). Increasing the treatment temperature from 300 °C to 500 °C lead to a better crystallisation with the growth of the nanocrystals [13, 16] as indicated by the decrease of the peaks width; the Full Width at Half Maximum (FWHM) of the anatase main peak decrease from 12 cm^{-1} to 9 cm^{-1} at 500 °C [16].

In Fig. 4 are shown the Raman spectra of the powders with high iron contents. The Raman spectrum of the powders Fe : Ti = 0.5 : 1 at 300 °C is typical of an amorphous material, but with the main feature centred at the same frequency of the anatase main peak; at 500 °C we observe all the anatase main bands and small pseudobrookite features at 200-230-340-660 cm^{-1}. The powders Fe : Ti = 1 : 1 at 300 °C show a large peak which indicates the presence of very small anatase nanocrystals, while at 500 °C the bands of anatase, hematite [17–21] and pseudobrookite are distinguishable. At higher iron content (Fe : Ti = 1.5 : 1) the hematite is visible in the Raman spectra also at low temperature, together with pseudobrookite and anatase at lower proportion. At 500 °C pseudobrookite and hematite are the crystalline phases observed in the Raman spectrum. In the case of Fe : Ti 1 : 1 and Fe : Ti 1.5 : 1 at both treatment temperature, the relative intensity of the Raman peaks of the different phases strongly varies with the powder grains on which the measurement is performed and also with the position of the laser spot on the same grain; at the highest Fe content we found positions in which the Raman spectrum corresponds to pure pseudobrookite. This means that there is a micrometric-scale phase segregation for that preparation. This is not true for the films: micro-Raman mappings (not reported here) show that the iron-titanium-oxide films prepared by dip-coating have a very good homogeneity also on the microscopic scale.

The results obtained starting with iron nitrate and TPOT in ethanol have been compared with those obtained by Macek *et al.* [14]. In the powders at 500°C at Fe : Ti = 0.5 : 1 and 1 : 1 they found the rutile phase for TiO_2 and pseudobrookite; for Fe : Ti = 1.5 : 1 they found rutile and hematite. Our results show anatase instead of rutile and the hematite is present at Fe : Ti = 1 : 1. We have no explanation for this difference, but often in the sol gel technique small changes in the preparation of the samples, not always reported, are responsible for the differences in the properties of the obtained materials, like the temperatures at which occur the phase transformations.

Many differences are observed in the thermal behavior between the powders and the thin films; further work is needed to understand if the differences are due to the different thermal treatments, to the interaction with the substrate for the film, to geometric differences, or other parameters. In particular, the pseudobrookite (Fe_2TiO_5) phase is more easily obtained in the films whereas in the powders heterogeneous mixtures of iron (hematite) and titanium (anatase) oxides are more easily obtained. A nearly complete pseudobrookite phase, obviously, is obtained in both powders and films, especially with Fe : Ti = 1.5 : 1. In addition, the comparison with the spectra of the natural pseudobrookite crystals shows that in the films the pseudobrookite crystals are not oriented.

The width and frequency shift of the anatase peaks are highly sensitive to the lack of long-range order (also due to dimensional effects) in the titania phase [13, 16, 22]; in the Fe : Ti powders with high iron contents, we observe an increase of the FWHM (from 9 to 18 cm^{-1} at 500 °C) and in the wavenumber (from 141 to 149 cm^{-1}) of the anatase main peak with increasing the iron content, indicating a larger disorder in the titanium oxide.

3.2. Low Fe concentrations

The Raman spectrum of the dried gel with 2% Fe (Fig. 5) shows an amorphous structure with organic residuals. The powders remain amorphous up to 300 °C. At 400°C the anatase phase appears and remains the only crystallised phase up to 700°C. At 800 °C and 900 °C only the rutile phase is obtained. The thermal behaviour is thus similar to that of the undoped titania [15]. Phases due to Fe are not revealed by Raman spectra. The XRD spectra of the powder (not reported) confirm the presence of the only anatase phase in the powders treated at 600°C but at 800 °C indicate, in addition to the rutile features, also a weak signal which can be assigned to (220) and (230) reflections of pseudobrookite.

The powders doped with 5% Fe, as indicated by the Raman spectra (Fig. 6), are already crystallised into anatase phase at the treatment temperature of 100°C.

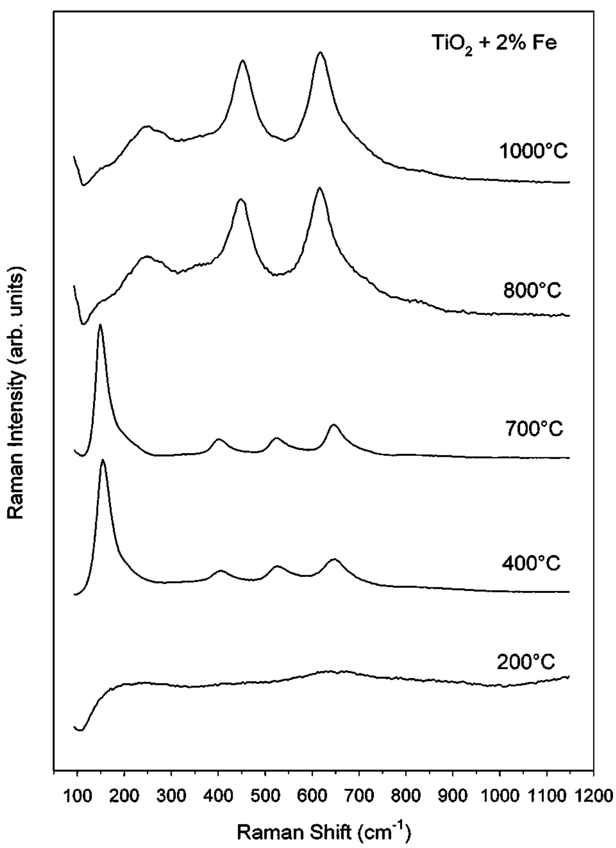

Figure 5 Raman spectra of the titania powders doped with Fe at 2%.

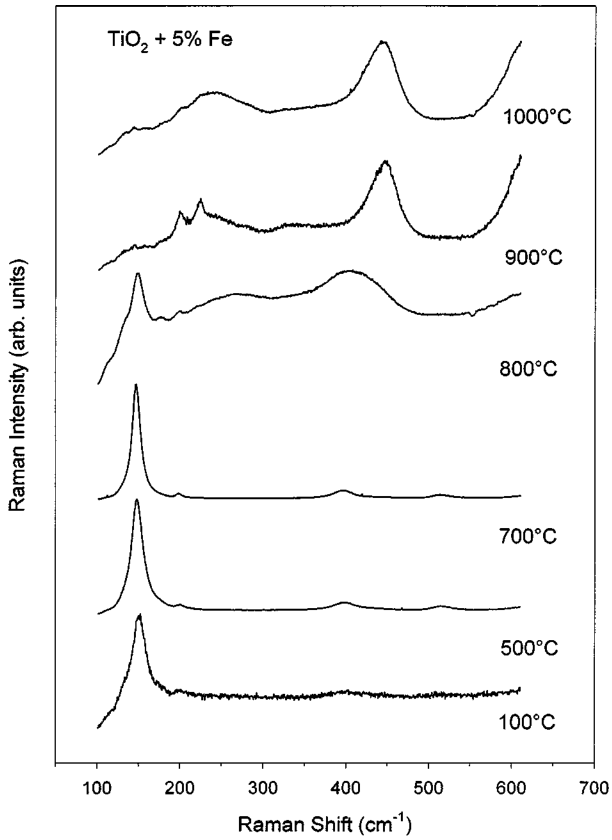

Figure 6 Raman spectra of the titania powders doped with Fe at 5%.

The crystallisation of the anatase proceeds as T increases (and the width of the Raman lines decreases) up to 700°C. No crystalline phase containing iron is observed up to this temperature. At 800°C the Raman spectrum shows broadened and shifted rutile features, with traces of some band of the pseudobrookite phase at about 200 cm^{-1}. The powders treated at 900° and 1000 °C show the typical features of a main rutile phase, together with minor pseudobrookite. The XRD spectra confirm these results.

The Raman spectra of the samples containing iron at 10% (Fig. 7) show the broad amorphous like features with organic peaks due to the solvent in the high frequency region (not reported in Fig. 7) at 100–200 °C. The crystallisation of anatase starts at 200 °C and is complete at 500 °C. At 600 °C the pseudobrookite is observed and the transition from anatase to rutile takes place at about 700–800 °C, where the intensity of the pseudobrookite peaks is also enhanced.

An overall broadening of the Raman peaks of the anatase and rutile is observed with increasing iron content, an effect which may be again explained by an increased disorder induced by the presence of Fe atoms. At the present the role of the iron is not completely clear: the disorder may be due to the inclusion of iron ions in the titania network or could be related to lower sizes of the titania nanocrystals; the presence of impurities at the grain boundaries (iron species) may slow down the growth of the titania grains [23, 24]. The last hypothesis seems to be contradicted by the fact that the crystallisation of the anatase is observed at temperatures lower than those reported in literature for pure TiO_2 [15], even if no clear dependence on the iron content of the

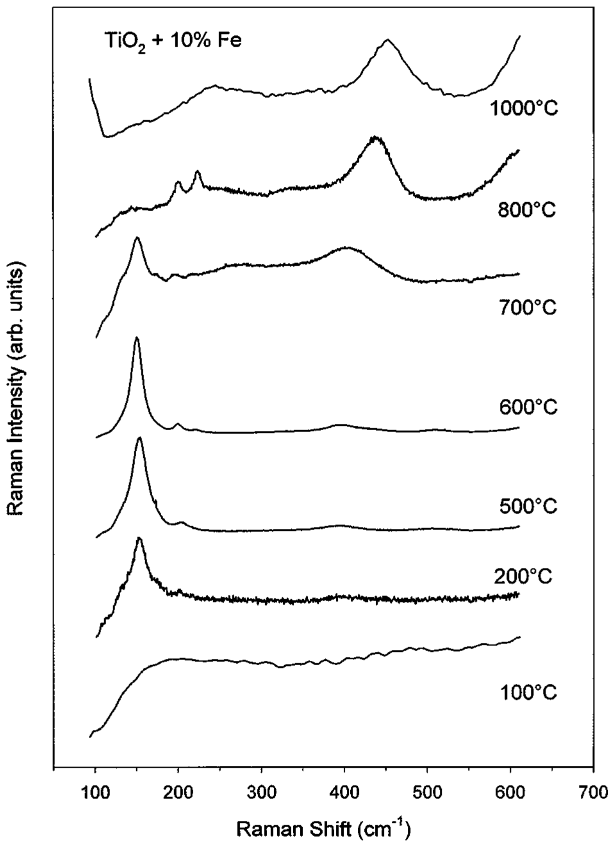

Figure 7 Raman spectra of the titania powders doped with Fe at 10%.

crystallisation temperature is observed. A definite trend with the amount of the dopant is not observed also for the anatase to rutile transformation temperature.

4. Conclusions

The sol-gel technique enables one to obtain a series of mixed iron-titanium oxides, both as powders and homogeneous thin films. Different thermal behaviors are shown by the powders and the films. At higher Fe concentrations the pseudobrookite is the prevalent, and in some cases the only, crystalline phase. The crystals of pseudobrookite are not oriented. No traces of ilmenite are found in the spectra, both in films and in powders, as expected from the oxidation state 3+ of the iron ions, favouring the formation of the pseudobrookite.

At low iron concentration in titania, the crystallization temperature of anatase is lowered, while no clear trend is observed as concerns the anatase to rutile transformation. The anatase Raman peaks are broadened with increasing iron content indicating an increased disorder in the titania network.

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