

# Thermal Evolution of Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> Sol–Gel Thin Films

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(Received 16 April 1991; accepted 21 May 1991)

## Abstract

Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> thin films were deposited on silica glass slides using three sol–gel solutions containing Ti–butoxide and different iron oxide precursors. The thermal evolution of the coatings was followed by DTA–TGA and XRD from 200 to 1000°C. All the iron-containing samples were amorphous up to 700°C, when a phase separation between iron and titanium oxides was evidenced by the presence of crystalline Fe<sub>2</sub>O<sub>3</sub>. Above that temperature a titanate compound (pseudobrookite) formed according to the equilibrium phase diagram. The use of different precursors did not affect the thermal evolution and all the different samples exhibited the same trend.

Auf SiO<sub>2</sub>-Glasplättchen wurden mittels dreier Sol–Gel–Lösungen aus Ti–Butoxid und unterschiedlichen Eisenoxidprecursoren dünne Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub>-Schichten erzeugt. Das thermische Verhalten der Schichten wurde im Temperaturbereich von 200°C bis 1000°C mit Hilfe der DTA, TGA und XRD untersucht. Bis 700°C waren alle eisenhaltigen Proben amorph. Bei 700°C fand eine Phasentrennung zwischen den Oxiden statt, was durch das Auftreten kristalliner Fe<sub>2</sub>O<sub>3</sub> nachgewiesen werden konnte. Über dieser Temperatur bildete sich gemäß dem Phasendiagramm eine Titanat-Verbindung (Pseudobrookit). Die Verwendung verschiedener Precursor hatte keinen Einfluß auf das thermische Verhalten; alle Proben zeigten die gleiche Tendenz.

On a déposé des films fins de Fe<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> sur des lamelles de silice en utilisant trois solutions sol–gel

différentes, contenant du butylate de titane et différents précurseurs d'oxyde de fer. L'évolution thermique des couches minces a été suivie par ATD–ATG et XRD de 200 à 1000°C. Tous les échantillons contenant du fer sont amorphes jusqu'à 700°C, tandis qu'une séparation de phase entre le fer et les oxydes de titane est mise en évidence par la présence de Fe<sub>2</sub>O<sub>3</sub> cristallin. Aux températures plus élevées, il se forme un composé à base de titane (pseudobrookite), conformément au diagramme de phase à l'équilibre. L'utilisation de différents précurseurs n'affecte pas l'évolution thermique, tous les échantillons présentent la même tendance.

## 1 Introduction

Oxide coatings based on the TiO<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub> system may be deposited on flat glass to give optical properties interesting for practical applications. As reported by Schroeder<sup>1</sup> the UV absorption edge of TiO<sub>2</sub> can be shifted at higher wavelengths, without decreasing its steepness, by admixing other metal alkoxides, such as those of Ni, Fe or Co. In these combinations the formations of compounds (titanates) are said to be responsible for the change of the characteristic absorption of the pure metal oxides.

In this sense TiO<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub> coatings could be applied on flat glass to increase its protection against near-UV radiation without decreasing significantly the visible transmittance.

In a previous paper<sup>2</sup> TiO<sub>2</sub>–Fe<sub>2</sub>O<sub>3</sub> thin films were deposited on soda-lime glass slides from different solutions and transmittance curves were studied as a

function of film thickness. The same solutions were also used to prepare bulk gels which were studied from the point of view of crystallization behaviour<sup>3</sup> and by Mössbauer spectroscopy to try to elucidate the structural evolution upon heating.<sup>4</sup>

In this work the thermal evolution of thin TiO<sub>2</sub> and TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> films deposited on silica slides was studied between 200 and 1000°C, following their weight loss, thickness shrinkage and crystallization. A comparison between films and previously studied powders is presented.

## 2 Experimental

Three solutions for the preparation of Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> gels with a Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> molar ratio of 0.15 were prepared using three different precursors for iron oxide: (I) Fe(C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>)<sub>3</sub>; (II) Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O; (III) Fe(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>; Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> was used as precursor for TiO<sub>2</sub>. It was dissolved in ethanol with acetylacetonate (AcAc/TiBut molar ratio=0.5) and the correct amount of iron precursor was added. Two other solutions were also prepared by mixing Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> and ethanol with acetylacetonate (AcAc/TiBut molar ratio=0.5) (IVa) and without acetylacetonate (IVb); all the solutions had a concentration of 10 g of oxides per litre. Silica glass slides were used as substrate. In order to get a reasonable thickness for the analyses (about 2000 Å), a multi-dipping coating procedure was adopted. After each deposition and before the next one the coated slides were treated for 15 min at 200°C.

The samples were then fired with a 15-h-long, 100°C step schedule from 200 to 1000°C introducing them directly into the hot furnace. After each step the thickness of the coatings was measured by a stylus apparatus. The thermal transformations of the films were followed by TGA and DTA and the crystallinity was detected by X-ray diffraction

(35 kV, 30 mA, CuK<sub>α</sub> radiation) with a conventional  $\theta$ -2 $\theta$  Bragg-Brentano goniometer.

Selected angular ranges were step-scanned several times until reaching a satisfactory signal-to-noise ratio. The instrumental function was determined with a  $\alpha$ -SiO<sub>2</sub> sample free from crystal size and lattice disorder. For the microstructural characterization an improved profile fitting method<sup>5</sup> using a pseudo-Voigt representation for the line profiles was used.

## 3 Results

### 3.1 Thermal analyses

The analyses were performed on powders obtained from unheated gelled films. In Figs 1–4 are reported the curves for the different samples, obtained using the same amount of powder.

The DTA data showed for all the systems containing acetylacetonate a complex exothermic pattern in the temperature range 150–400°C, which was almost completely absent in sample IVb. It can be noticed that weight losses were associated with each exothermic peak.

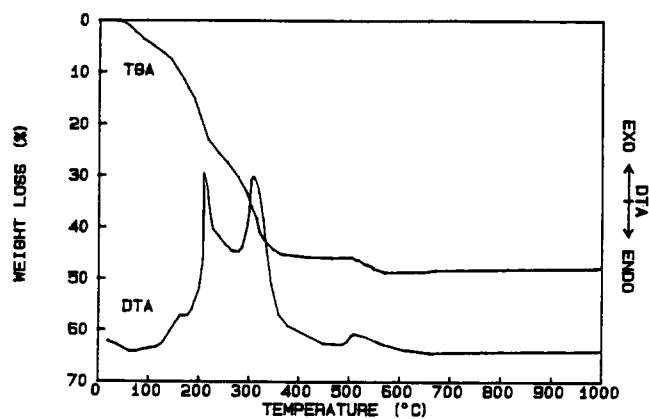


Fig. 2. DTA and TGA curves of sample II. Heating rate 10°C/min.

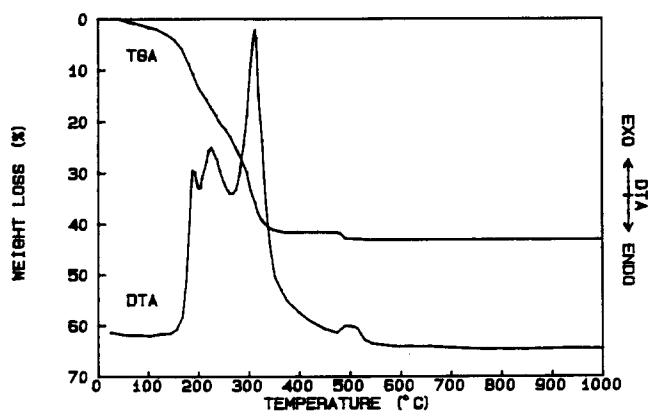


Fig. 1. DTA and TGA curves of sample I. Heating rate 10°C/min.

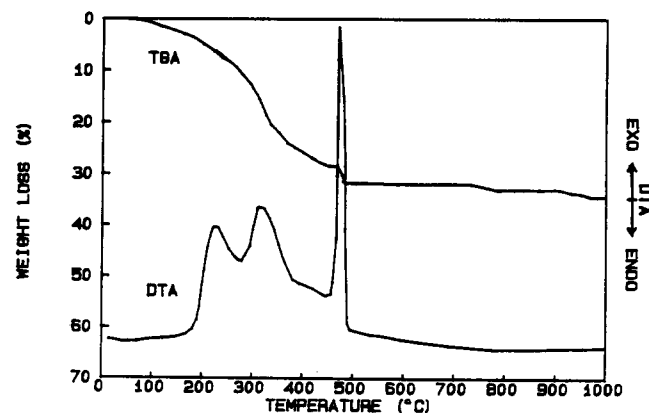


Fig. 3. DTA and TGA curves of sample III. Heating rate 10°C/min.

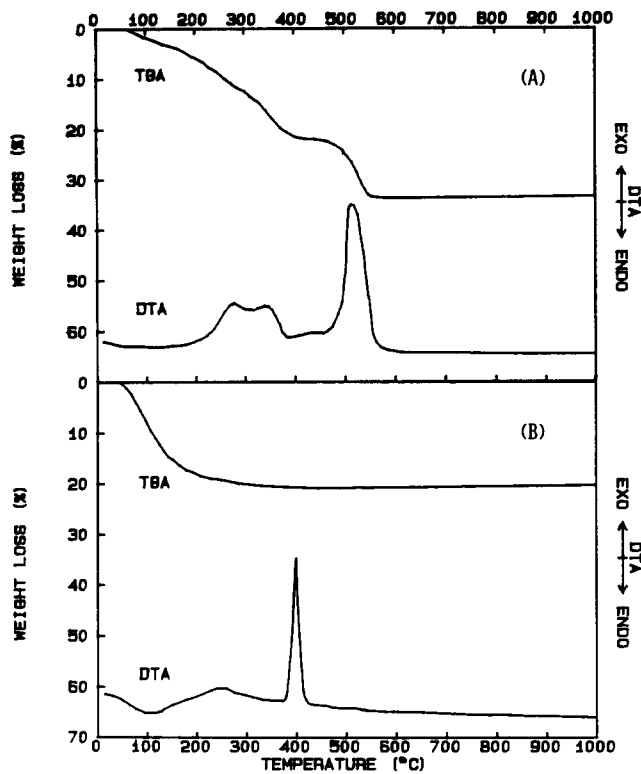


Fig. 4. DTA and TGA curves of sample IVa (a) and IVb (b). Heating rate 10°C/min.

An exothermic effect at around 500°C was also exhibited by all acetylacetonate containing samples, whose intensity and sharpness varied from case to case. It was associated with a weight loss. A different exothermic peak was present in both samples IVa and IVb (particularly in IVb) not related to any weight loss, due to the crystallization of anatase.

### 3.2 Film thickness and shrinkage

Film thicknesses ranged from 3000 Å, for samples at 200°C, to 1500 Å, after heating at 1000°C. The shrinkages are reported in Fig. 5. All the four different systems exhibited the same behaviour.

In the temperature range 200–400°C there was the maximum contraction (about 20%), clearly associated with the weight losses previously described.

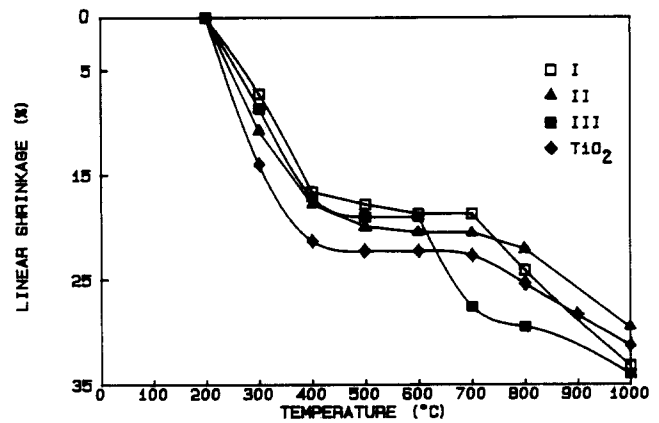


Fig. 5. Linear shrinkages of different samples.

Between 400 and 600°C there was a very slight contraction which does not seem proportional to the weight losses recorded for the different samples. In this range of temperatures sample I, for instance, had a 1.4% contraction and a 44% weight loss (at 505°C), while sample II had a 2.4% contraction and a 5% weight loss (at 510°C). For temperatures over 600°C all the samples showed an average contraction of 10–15%, although there were not any weight losses.

### 3.3 X-ray diffraction

As described in the experimental section, the samples were fired from 200 to 1000°C at steps of 100°C, and analysed after each step. Samples I, II and III, which contain iron oxide, showed the same trend and did not present any crystallization phenomena until 700°C, when haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) and rutile (TiO<sub>2</sub>) appeared. At 800°C, due to a solid state reaction, pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>) formed and haematite disappeared. A typical set of XRD patterns, relative to sample III, is shown in Fig. 6. In TiO<sub>2</sub> samples anatase and rutile appeared at 400°C and 900°C respectively.

The average crystallite sizes were calculated using the Scherrer equation<sup>6</sup> and are reported in Table 1. In Table 2 are reported semiquantitative data for the

Table 1. Average crystallite size

Temperature (°C)	I			II			III			IVa	
	H	PB	R	H	PB	R	H	PB	R	A	R
400	—	—	—	—	—	—	—	—	—	163	—
500	—	—	—	—	—	—	—	—	—	166	—
600	—	—	—	—	—	—	—	—	—	236	—
700	250	—	115	180	—	136	200	—	129	320	—
800	—	298	198	—	342	183	—	233	271	381	—
900	nm	nm	nm	nm	nm	nm	nm	nm	nm	432	579
1000	—	352	420	—	276	377	—	342	382	511	543

H, haematite ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>); PB, pseudobrookite (Fe<sub>2</sub>TiO<sub>5</sub>); R, rutile (TiO<sub>2</sub>); A, anatase (TiO<sub>2</sub>); nm = not measured.

Table 2. Area of peaks

Temperature (°C)	I			II			III			IVa	
	H	PB	R	H	PB	R	H	PB	R	A	R
400	—	—	—	—	—	—	—	—	—	s	—
500	—	—	—	—	—	—	—	—	—	s	—
600	—	—	—	—	—	—	—	—	—	s	—
700	w	—	m	vw	—	m	vw	—	w	vs	—
800	—	w	s	—	w	s	—	w	w	vs	—
900	nm	nm	nm	nm	nm	nm	nm	nm	nm	w	w
1000	—	w	ws	—	w	vs	—	w	m	vw	vs

vw, very weak (0–20 arbitrary units); w, weak (20–40); m, medium (40–60); s, strong (60–80); vs, very strong (80–100); nm, not measured.

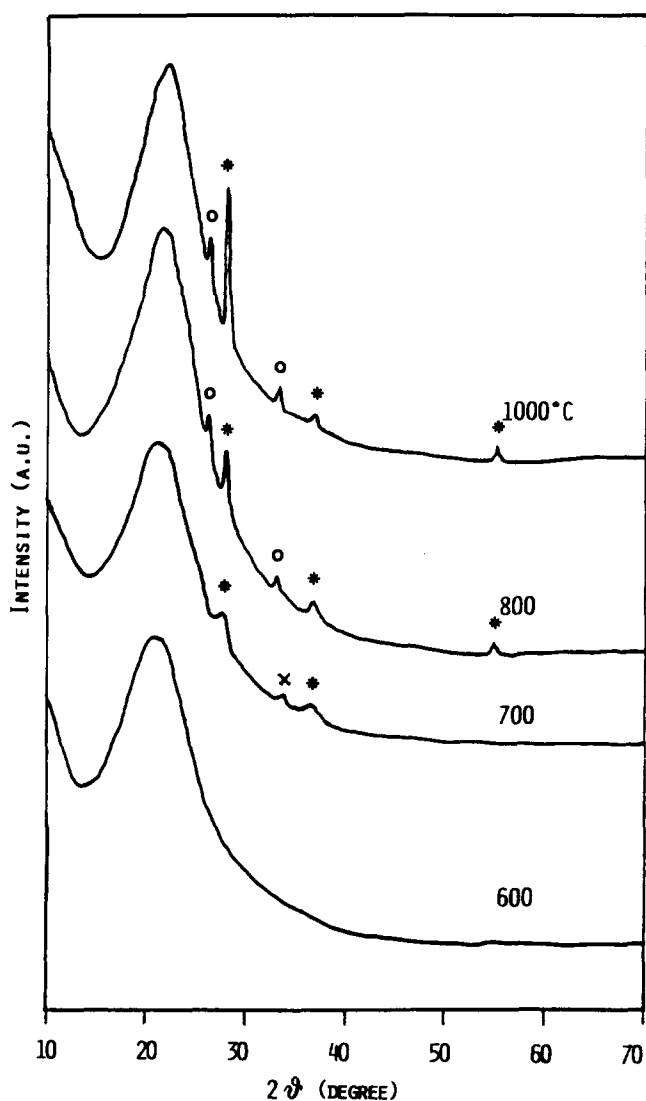


Fig. 6. XRD patterns of sample III. Heating time 15 h. ×, haematite; \*, rutile; ○, pseudobrookite.

corresponding peak areas, calculated after fitting the experimental peak profiles by a pseudo-Voigt function. After the instrumental correction, the integral breadth  $\beta$  is given by:

$$\beta = \omega \left[ n\pi + (1-n) \sqrt{\frac{\pi}{\ln 2}} \right]$$

where  $n$  and  $\omega$ , adjusted parameters, are the Cauchy content and the half-width at half-maximum respectively.

#### 4 Discussion

All the samples in the range 20–150°C exhibited a weight loss associated with an endothermic effect of different intensity, due to desorption of physically adsorbed water and of residual solvent. The weight losses and the exothermic peaks recorded between 150 and 400°C and at 450–550°C for all but the IVb samples indicate that residual organic groups are present in acetylaceton containing gels. This is not surprising, because it is known that acetylaceton bonded to titanium is difficult to remove by hydrolysis, even with a large excess of water, and prevents condensation.<sup>7</sup> In this respect it is also interesting to observe that the peak at 400°C attributed to the crystallization of anatase from the amorphous gel is much more intense and sharp in sample IVb where acetylaceton was not added.

A large reduction (if not an absence) in this exothermic peak can be observed in the samples containing  $\text{Fe}_2\text{O}_3$ . In fact, from the XRD data (see Table 1) a strong difference between the systems I, II and III and samples IVa and IVb is evident. The titanium oxide crystalline form anatase was not present at all in the first three samples, indicating a hindering effect of  $\text{Fe}_2\text{O}_3$  towards  $\text{TiO}_2$  crystallization at low temperatures. Rutile, in agreement with the Ti-O phase diagram<sup>8</sup> appeared only at 700°C, while in samples IV the anatase–rutile transformation shifted to 800°C. A hindering effect of iron was also observed in the polycondensation process of an alkoxide-derived titania sol.<sup>9</sup>

The  $\text{TiO}_2$ – $\text{Fe}_2\text{O}_3$  system, investigated by Karkhanavala & Momin,<sup>10</sup> has a single stable binary compound,  $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$  (pseudobrookite). The

composition chosen in this work should give rise to  $Fe_2O_3 \cdot TiO_2$  and  $TiO_2$  as stable phases.

In samples I–III  $Fe_2O_3$  and  $TiO_2$  were present as separated phases and reacted to give the stable compound  $Fe_2TiO_5$  only at 800°C. All the systems exhibited the same behaviour indicating that, regardless of the iron precursor used, the formation of the iron titanate was not achieved by chemical synthesis at low temperature.

The problem of homogeneity in multicomponent gel systems has been much debated. It is known that the achievement of a clear starting solution is not sufficient to assure homogeneity in the resulting gel, as it depends on the precursor reactivities. In this work different precursors for iron oxide were used, but in all cases haematite formed as a separate phase, indicating that homocondensation was not prevented.

In a previous work<sup>3</sup> bulk gelation of solutions I, II and III was obtained in a closed system after addition of water (group A) and in a system open to the atmosphere without water in solution (group B). In the first case solutions gelled without losing solvent but in different ways depending on the iron precursor: gelation followed by syneresis (III), flocculation (II), gelation without syneresis (I). In group B gelation was faster than in group A due to evaporation of solvent, though the only available water was that from moisture. The powders obtained exhibited separation of haematite in all cases but sample III of group B, where anatase formed at 500°C and pseudobrookite plus rutile were observed to form after treatment at 1000°C. In this work thin films were prepared in such a way that gelation was similar to procedure B.

Karkhanavala & Momin,<sup>10</sup> studying the  $TiO_2$ - $Fe_2O_3$  system under hydrothermal conditions, in the composition range close to our  $Fe_2O_3/TiO_2$  ratio found haematite, anatase and a compound,  $Fe_2O_3 \cdot 3TiO_2$  (arizonite), whose X-ray pattern is very similar to that obtainable with a mixture of  $\alpha$ - $Fe_2O_3$  and anatase. This compound, which was shown to be metastable under atmospheric conditions at temperatures above 500°C, was not detectable in our X-ray patterns (see Fig. 6). Thus it is interesting to observe that the low temperature formation of  $Fe_2O_3 \cdot TiO_2$ , whatever might be the reason, is not an easy task. As far as the optical applications of these coatings are concerned, it should be observed that the heat treatment of coated soda-lime sheets must be performed at temperatures lower than those required for pseudobrookite formation. Thus the optical properties measured in our previous work<sup>2</sup> cannot be at-

tributed to crystalline iron titanate. Looking at the crystallization path of the amorphous phase, even a disordered structural arrangement of iron resembling that one of pseudobrookite seems unlikely.

The comparison between films and powders allows us to observe some differences in their crystallization behaviour. As reported in Ref. 3, group A gels exhibited crystallinity at 100°C, while group B gels did not show any crystalline phase until after 500°C. In particular was recorded the formation of anatase in the temperature range 100–500°C—depending on the gelling procedure and on the system—and its complete transformation into rutile after heating at 1000°C. Furthermore, samples obtained from solution II exhibited a strong difference from the others in crystallization behaviour, showing the formation of  $Fe_2O_3$  and  $Fe_2TiO_5$  without any presence of crystalline  $TiO_2$  at every temperature.

Both group B powders and films exhibited a delay in the formation of crystalline species. However crystallinity developed in the films only at 700°C, while in group B powders it was present at 500°C, showing that crystallization was more difficult in coatings, likely due to the fact that films have a lower surface area than bulk gels.<sup>11</sup>

The differences observed in the crystallization of powders and films obtained from the same solutions could also be related to the complex effects that chemical reactions and solvent evaporation have on the gel structure, but this point, which is of general interest, should be better investigated in the future.

As far as film shrinkage is concerned, the general trend observed in  $TiO_2$  and  $TiO_2$ - $Fe_2O_3$  gels was first a contraction between 200 and 400°C followed by a temperature range with a constant film thickness and by a second contraction. The first thickness decrease was associated with the weight losses occurring in the same temperature interval. The second one, at temperatures higher than 600°C, cannot be related to any mass loss, as the weight remains constant. Therefore it should be related partly to the sintering of the films and partly to the change in density due to the transformation anatase  $\rightarrow$  rutile. This transformation, in fact, takes place above 700°C and, in a film of pure titanium oxide, should cause a thickness contraction of about 10%, going from a theoretical density of 3.84 g/cm<sup>3</sup> (anatase) to a density of 4.26 g/cm<sup>3</sup> (rutile).

It can be noticed, also, that sample III exhibited a faster tendency towards densification, probably due to the earlier elimination of organic residuals (see DTA-TGA patterns).

## 5 Conclusions

Thin 0.15 Fe<sub>2</sub>O<sub>3</sub>·TiO<sub>2</sub> coatings were deposited on silica slides from sol-gel solutions containing different iron oxide precursors. The thermal evolution was investigated by DTA-TGA, XRD and thickness shrinkage.

As far as the crystallization behaviour is concerned, the results of this work may be summarized as follows:

- (a) It was found that iron oxide inhibits TiO<sub>2</sub> crystallization.
- (b) The phase diagram Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> indicates, for the composition prepared in this work, Fe<sub>2</sub>TiO<sub>5</sub> and TiO<sub>2</sub> as stable phases. Instead, regardless of the iron precursor used, we found the formation of haematite, followed by the crystallization of Fe<sub>2</sub>TiO<sub>5</sub>, only at 800°C. This fact can be attributed to the homocondensation reactions of the iron oxide and the titanium oxide precursors.
- (c) Differences between crystallization of powders and films of the same composition and obtained from the same solutions were observed. In particular crystallization in films was shifted toward higher temperatures.

The shrinkage versus temperature behaviour of the films indicates that at 600°C densification is not completed. This fact should be taken into account when looking at the optical applications of these coatings deposited on soda-lime glasses.

## Acknowledgement

Research was supported by 'Progetto Finalizzato Materiali Speciali per Tecnologie Avanzate del Consiglio Nazionale delle Ricerche'.

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