Journal of Thermal Analysis and Calorimetry, Vol. 66 (2001) 37–46

THERMAL AND MICROCHEMICAL CHARACTERISATION OF SOL-GEL SiO_2, TiO_2 AND $x$$SiO_2$–(1–$x$)$TiO_2$ CERAMIC MATERIALS

G. M. Ingo[1]*, C. Riccucci*[1]*, G. Bultrini*[2]*, S. Dirè*[3] *and G. Chiozzini*[1]

[1]CNR, Istituto di Chimica dei Materiali, CP 10, 00016 Monterotondo Stazione, Roma, Italy
[2]Dipartimento di Chimica, Università di Catania, v.le A. Doria 6, 95125 Catania, Italy
[3]Dipartimento Ingegneria dei Materiali, Università di Trento, 38050 Mesiano-Trento, Italy

Abstract

Amorphous SiO_2, TiO_2 and $x$$SiO_2$–(1–$x$)$TiO_2$ ceramic materials with selected values of x 0.5, 0.7 and 0.9, have been prepared via sol-gel process using silicon tetraethoxysilane (TEOS) and titanium tetraisopropoxide Ti(OPri)$_4$. By means of the combined use of differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES), the surface microchemical structure and morphology of the sol-gel materials have been studied as a function of thermal treatments carried out in air up to 1200°C. In the range of temperature from 50 to 450°C, DTA-TG results evidence a remarkable mass loss due to the evaporation of organic solvents entrapped in the sol-gel materials and of the remnant organic components of the precursor metal alkoxides. In the range of temperature from 400 to about 1000°C, by means of the combined use of DTA, XRD, XPS and XAES techniques as a function of temperature and of chemical composition, it is possible to evidence the formation of crystalline phases such as quartz, anatase and rutile. Furthermore, lineshape analysis of O 1s XPS peak allows to distinguish between single O–Ti and O–Si bonds and also to disclose the presence of cross linking Si–O–Ti bonds, that act as bridges between SiO_2 and TiO_2 moieties. As a function of temperature, Si–O–Ti bonds are broken and the formation of new Ti–O and Si–O bonds as in TiO_2 and SiO_2 takes place as well as a silica segregation phenomenon.

Keywords: DTA-TG, microchemical structure, oxide ceramic materials, SEM, silica, sol-gel processing, surface, titania, XPS

Introduction

The low-temperature sol-gel synthesis of glasses and ceramic materials received considerable scientific and technological interest during the last years [1–8]. Indeed, starting from liquid molecular precursor, it is possible to produce via hydrolysis-condensation reactions, a great variety of unusual multication ceramic oxide materials, the chemical composition and structure of which can be tailored by the chemical design of molecular precursors and synthesis parameters. Furthermore, the sol-gel synthesis offers opportunities for producing also fine ceramic powders with a high

1418–2874/2001/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

surface area and high purity as well as films and coatings with tailored chemical and physical features.

By means of the combined use of differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS) and X-ray induced Auger electron spectroscopy (XAES), SiO_2, TiO_2 and $x$$SiO_2$–(1–$x$)$TiO_2$ sol-gel ceramic materials, with selected values of x 0.5, 0.7 and 0.9, have been studied for identifying the variations of the microchemical and microstructural structure as a function of temperature including temperature dependent changes of the surface chemical composition, bonding and structure.

Experimental

SiO_2–TiO_2 ceramic materials were prepared at room temperature (r.t.) according to the experimental procedure reported in reference [3–7]. The method is based on the use of a solution of tetraethoxysilane (TEOS) with absolute ethanol (EtOH) and water in the molar ratio TEOS:EtOH:H_2O=1:2:1 adjusting the pH of water at 1 by adding hydrochloric acid. After stirring the solution for 6 h, titanium tetraisopropoxide (TIPR) was added. The sol was poured in an open vessel and the sol-gel transition took place in three days. The gel was then dried at r.t. for seven days. SiO_2 was obtained from TEOS:EtOH:H_2O=1:2:1 solution according to the above mentioned conditions. TiO_2 was prepared by adding water to TIPR under stirring for 2 h. The TiO_2 precipitate was filtered, washed with distilled water and dried at 80°C.

DTA-TG measurements were carried out in air from room temperature to 1200°C using an automated thermal analyser (Stanton Redcroft STA-781) at a heating rate of 10°C min^{-1}.

The samples for XPS and XRD analysis were prepared first drying the sol-gel materials at room temperature for seven days and then air heating them to the desired temperature with a heating rate of 10°C min^{-1} and maintaining the samples at the selected temperature for 2 h.

XPS study was carried out on an Escalab Mk II spectrometer using $MgK_{\alpha1,2}$ radiation as excitation source ($h\nu$=1253.6 eV). The electron hemispherical analyser was operated in fixed analyser transmission mode (FAT) by selecting a constant pass energy of 20 eV. Under these conditions, the full width at half maximum (FWHM) of argon ion cleaned Ag $3d_{5/2}$ line was 1.0 eV. Binding energies (BEs) were referenced to the Fermi level of the analyser and confidence in the linearity of BE scale was based upon setting the position of Au $4f_{7/2}$, Cu $L_3M_{45}M_{45}$ and Cu $2p_{3/2}$ peaks at 84.0, 567.8 and 932.5 eV, respectively. Corrections for the energy shift, due to the steady state charging effect, were accomplished by assuming the C 1s line, resulting from the adsorbed hydrocarbons, as lying at 285.0 eV. Furthermore, on pure sol-gel SiO_2 and TiO_2 powders, 20 nm thick gold film has been deposited to provide an Au $4f_{7/2}$ BE reference. As previously observed by other authors [9], two different charging corrections procedures result in essentially identical BE data. Reproducibility in the results was ±0.15 eV. XRD patterns were recorded directly on the powders by multiple scanning using an automated Seifert XRD-3000 diffractometer. The identification of the species was carried out by using a Seifert XDAL 3000 Software Index I. SEM and EDS characterisation was carried out by using a Cambridge 360 scanning electron microscope equipped with an EDS apparatus and a LaB_6 filament.

Results and discussion

Figure 1 shows the micromorphology of the $50SiO_2$–$50TiO_2$ and $90SiO_2$–$10TiO_2$ sol-gel materials in as prepared conditions after grinding (hereafter a.p.) and after an air thermal treatment (t.t.) carried out at 1000°C for 2 h in air, micrographs A, C, B and D, respectively. Under these experimental conditions, the back scattered electrons (BSE) images do not disclose evidence of an appreciable variations of the morphology in the as prepared sol-gels as a function of the chemical composition. Furthermore, BSE images show that the air thermal treatment at 1000°C induces only the formation of cracks and of small particles scattered on the surface of the particles.

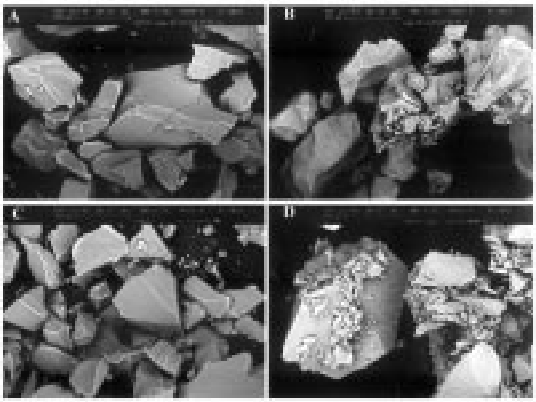

Fig. 1 Back scattered electrons (BSE) images that show the micromorphology of the $50SiO_2$–$50TiO_2$ sol-gel ceramic in as prepared condition, of the $90SiO_2$–$10TiO_2$ sol-gel ceramic in as prepared conditions, of the $50SiO_2$–$50TiO_2$ sol-gel ceramic after an air thermal treatment at 1000°C and of the $90SiO_2$–$10TiO_2$ sol-gel ceramic after an air thermal treatment at 1000°C, micrographs A, C, B and D, respectively

DTA-TG curves for SiO_2, TiO_2 and $50SiO_2$–$50TiO_2$ materials are reported in Fig. 2 for showing the typical air thermal behaviour of the sol-gel material. Furthermore, in order to show the occurrence of crystallisation processes during the air thermal treatment, in Fig. 3 are reported some selected XRD patterns for TiO_2 after an air thermal treatment carried out for 2 h at 400, 800 and 1200°C.

In Table 1 are listed the binding energies (BEs, expressed in eV) of Si 2p, Ti $2p_{3/2}$, O 1s XPS peaks and XAES α' parameters [10,11] for as prepared and air thermal treated SiO_2, TiO_2 and SiO_2–TiO_2 sol-gels as well as for some reference compounds.

It is worth noting that XAES α’ parameter is obtained by means of the combined use of both the photoelectron and X-ray induced or Bremstrahlung Auger line according to:

$$\alpha' = KE_{(\text{Auger peak})} - KE_{(\text{photoelectron peak})} + h\nu$$

So conceived α’ has the advantages of being independent of photon energy, of always having positive values and is independent of the charge referencing operation. Therefore, α’ is found with higher accuracy than the determination of either photoemission line energy alone.

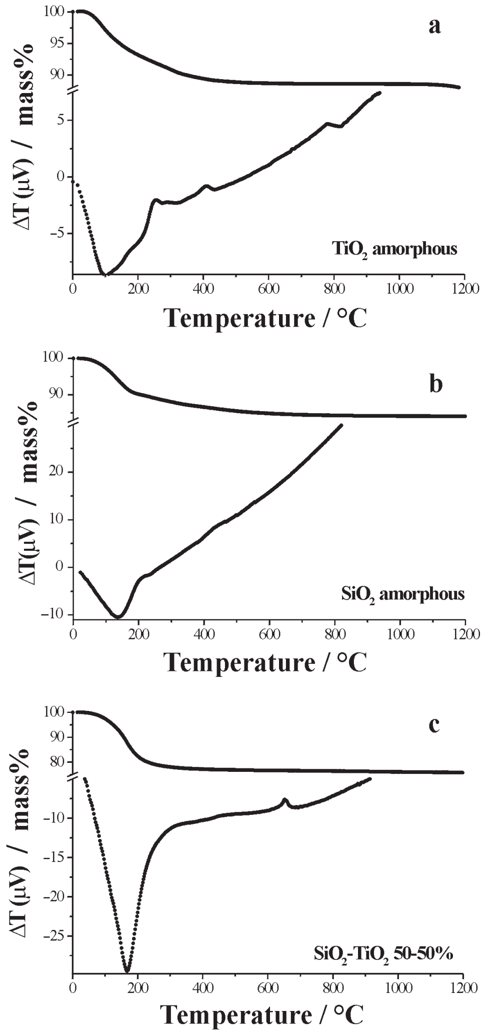

Fig. 2 DTA-TG curves for SiO_2, TiO_2 and $50SiO_2$–$50TiO_2$ sol-gel materials (air, heating rate 10°C min^{-1})

The surface chemical composition has been obtained also via XPS analysis and the presence of O, Si and Ti was monitored as well as a small amount of carbon only on the as prepared materials. The presence of this latter element indeed disappears after the first thermal treatment carried out at 400°C in air.

This phenomenon can be related to the TG curves reported in Fig. 2 that show an appreciable mass loss occurring in the temperature range from room temperature to 450°C as well as to the endothermic minima in the DTA curves. These results provide information on the evaporation of physically absorbed water and other solvents and on the cracking of organic compounds coming from the remnant contamination of the precursor solution. Indeed, the presence of these latter compounds in the as prepared samples is indicated by C 1s signals as well as from the lineshape analysis of the Ti $2p_{3/2}$ and Si 2p photoemission peaks (not shown). These latter signals are peaked at 459.2±0.1 and 103.3±0.1 eV, respectively and are slightly broadened on the low binding energy side. This asymmetry is due to the presence of Ti–O–$CH(CH_3)_2$ and Si–O–CH_2CH_3 bonds from the precursor solution and disappears when the sol-gel materials are subjected to air thermal treatments at 400°C.

At higher temperature, the line shape of XPS peaks Si 2p and Ti $2p_{3/2}$ peaks does not change appreciably thus indicating that the chemical bonds of silicon and titanium can be described as Ti^{4+} and Si^{4+} oxides [3]. Furthermore, we note that BEs for Ti $2p_{3/2}$ and Si 2p peaks, in some cases, slightly increase with increasing temperature, but this variation is within the experimental uncertainty.

It is worth noting that the organic compounds are removed with increasing temperature from the network of the sol-gel ceramic without inducing an appreciable variation of the surface micromorphology i.e. without forming pores observable via scanning electron microscopy (SEM).

With increasing temperature (higher than 400°C), other microchemical or microstructural changes could take place such as surface chemical composition variation and crystallisation phenomena of the sol-gel ceramic materials. Both are important phenomena associated with thermal treatment of sol-gel materials and these events have been followed by means of the combined use of DTA-TG, XRD and XPS-XAES techniques in the temperature region from about 400 to 1000°C.

DTA-TG curves shown in Fig. 2 for SiO_2, TiO_2 and $50SiO_2$–$50TiO_2$ powders, evidence thermal induced modifications disclosing exothermic peaks at different temperatures likely due to pyrolysis phenomena while TG curves do not show appreciable variations.

By combining XRD patterns, DTA curves and XPS-XAES results reported in Table 1, it is possible to establish that a main variation suffered by SiO_2, TiO_2 and $x$$SiO_2$–(1–$x$)$TiO_2$ sol-gel ceramics with increasing temperature is due to the variation of structure. In particular, XPS-XAES results indicate that the silicon and titanium α' Auger parameters for both SiO_2, TiO_2 and SiO_2–TiO_2 powders, vary as a function of the thermal treatment temperature from about 1711.5 to about 1712.0 eV, and from 871.9 to 873.2±0.2 eV, respectively. These latter changes are due to the crystallisation of amorphous SiO_2 and TiO_2 to quartz, anatase and rutile. Indeed, the comparison between XPS-XAES data for the sol-gel materials and the titanium α' Auger parame-

Table 1 Binding energies of Si 2p, Ti $2p_{3/2}$, O 1s photoemission signals and α' Auger parameters (expressed in eV) for as prepared (a.p.) and air thermal treated at 1000°C (t.t.) SiO_2, TiO_2 and $xSiO_2$–(1–x)TiO_2 sol-gel materials as well as for some reference compounds

Sample	O 1s	Si 2p	Ti $2p_{3/2}$	α'(Si)	α'(Ti)
TiO_2 a.p.	530.6 532.0	–	459.3	–	871.9
TiO_2 t.t. (1000°C)	530.6	–	459.3	–	873.1
SiO_2 a.p.	531.7 532.7	103.4	–	1711.4	–
SiO_2 t.t. (1000°C)	532.7	103.6	–	1712.0	–
$50SiO_2$–$50TiO_2$ a.p.	530.6 531.4 532.7	103.6	459.2	1711.4	871.9
$50SiO_2$–$50TiO_2$ (1000°C)	530.6 531.5 532.7	103.6	459.3	1712.0	872.8
$70SiO_2$–$30TiO_2$ a.p.	530.7 531.6 532.7	103.3	459.1	1711.6	871.8
$70SiO_2$–$30TiO_2$ (1000°C)	530.7 531.6 532.6	103.7	459.3	1711.9	873.1
$90SiO_2$–$10TiO_2$ a.p.	530.6 531.6 532.6	103.2	459.3	1711.6	871.5
$90SiO_2$–$10TiO_2$ (1000°C)	530.6 531.7 532.7	103.4	459.2	1711.9	873.4
SiO_2 (amorphous)	532.7	103.4	–	1711.3	–
SiO_2 (quartz)	532.7	103.5	–	1712.0	–
TiO_2 (rutile)	530.6	–	459.3	–	873.2
TiO_2 (brookite)	530.6	–	459.3	–	873.6
TiO_2 (anatase)	530.5	–	459.3	–	872.9

ter values for reference anatase, brookite and rutile crystals reported in Table 1, combined to DTA and XRD results, indicate that the amorphous TiO_2 changes its structure to the anatase form at about 420°C and to rutile at about 800°C. On the contrary, the titanium α' Auger parameter for $xSiO_2$–(1–x)TiO_2 powders as well as DTA curves and XRD patterns indicate that anatase is formed at about 600°C and maintains this crystalline structure up to 1000°C. These results reveal that the variation of the crystalline structure for $xSiO_2$–(1–x)TiO_2 sol-gel materials, takes place at different temperature and is related to the chemical composition of the sol-gel ceramics. It is worth noting that structural information obtained via XPS-XAES results are in good agreement with XRD results thus demonstrating that the surface structural modification occurs also in the bulk of the sol-gel materials. Furthermore, it is worth remarking that the α‘ titanium Auger parameter for as prepared $90SiO_2$–TiO_2 sol-gel material is 871.3 eV. This result could be related to a possible fourfold co-ordination of titanium in SiO_2–TiO_2 glasses with a TiO_2 content lower than 10 mol% [12]. Indeed, the calculations for α’ using the simple electrostatic model [10, 11], indicate that a titanium fourfold co-ordinated is characterised by an α’ value lower than the amorphous phase and the octahedral structure.

The other important variation induced by the thermal treatment could be the change of the chemical bonds for silicon and titanium that can be studied via XPS as a function of temperature.

The most interesting features are given by O 1s signal, the components of which are characterised by different BEs values. These latter data are reported in Table 1 and show large differences for SiO_2, TiO_2 and SiO_2–TiO_2 materials. Indeed, a ready distinction between SiO_2 and TiO_2 is achieved from O 1s lineshape analysis having these latter compounds largely different BE values and being clearly indicative of a mainly single chemical environment surrounding the photo-emitting oxygen. By way of contrast, $x SiO_2$–(1–x)TiO_2 sol-gel ceramics are characterised by complex profiles that are indicative of the presence of different oxygen chemical bonds. Curve fitting process has been then performed on O 1s spectra in order to quantify the presence of each chemical bonding in the composite bands that are indicative of the coexistence of different oxygen chemical bondings peaked at 531.4±0.1 eV, 530.6±0.1 eV and 532.7±0.1 eV. On the basis of the measurements carried out on pure TiO_2 and SiO_2 powders we assign the two latter components to Ti–O–Ti and Si–O–Si bonds. The first O 1s component centred at 531.4 eV, that has an intermediate BE value lying between the two extreme BEs, is assigned to Ti–O–Si bond. This assignment is proposed on the basis of previously reported considerations [13–15] on the system Fe_2O_3, SiO_2 and Fe_2SiO_4 systems where O 1s component pertinent to Fe–O–Si bond, has a BE value intermediate between Fe–O–Fe and Si–O–Si BEs.

As a function of temperature, O 1s spectra undergo striking modifications as the Ti–O–Si component decreases at temperature higher than 600°C and new O–Ti and O–Si bonds are formed, as long as O 1s spectrum for $x SiO_2$–(1–x)TiO_2 treated at 1000°C is characterised by a twofold line shape, consisting of a component centred at 530.6 along with a component at 532.7 eV. These latter values are exactly at the same BE as disclosed by all the one-component spectra for pure sol-gel titanium and silicon oxides. It is worth noting that these surface chemical bonding variations do not give rise to sharp exothermic or endothermic peaks in the DTA curves thus demonstrating that the chemical reactions take place only on the surface of the sol-gel ceramics or give rise to a low intensity and very broad signal along the whole temperature range from 400 to 1000°C.

The variation of the chemical bonding in $x SiO_2$–(1–x)TiO_2 materials as a function of temperature is associated also to the variation of the surface chemical composition. This change has been evidenced by the variation of Si/Ti atomic ratios ob-

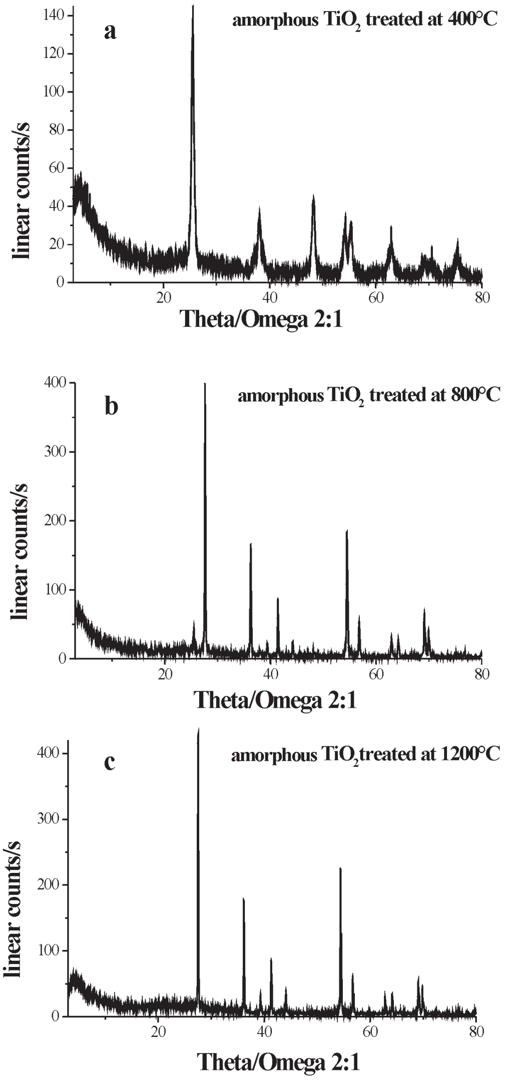

Fig. 3 Selected X-ray diffraction (XRD) patterns for TiO_2 sol-gel ceramic materials after an air thermal treatment carried out for 2 h at 400, 800 and 1200°C. The XR diffractrograms disclose the presence of anatase in the TiO_2 material after an air thermal treatment carried out for 2 h at 400°C, of rutile with a small amount of anatase for the TiO_2 sol-gel ceramic after an air thermal treatment carried out for 2 h at 800°C and of rutile for TiO_2 sol-gel material treated at higher temperature

tained via quantitative XPS analysis reported in Table 2. These latter Si/Ti atomic ratios are based on Ti $2p_{3/2}$ and Si 2p peaks and are compared in Table 2 with Si/Ti atomic ratios calculated from the intensity ratio measurements of O 1s single components. The data are in good agreement also with the chemical analyses and show that SiO_2 surface amount increases as a function of temperature. As already shown by other authors [16] in 60 mol% SiO_2–$40TiO_2$ glasses subjected to air thermal treatment at 1000°C, by means of transmission electron microscopy (TEM), a possible explanation of the change of the surface chemical composition could include a SiO_2 segregation and precipitation- agglomeration of TiO_2.

Table 2 Si/Ti surface atomic ratios for $x SiO_2$–$(1–x)TiO_2$ in as prepared conditions (a.p.) and after air thermal treatment (t.t.) carried out at 400, 600, 800 and 1000°C. The atomic ratios have been obtained from XPS quantitative analyses based on Ti $2p_{3/2}$ and Si 2p peaks (marked with an asterisk), and Si/Ti atomic ratios calculated from the intensity ratio measurements of the O 1s single components

Sample	Temperature/°C	Si/Ti*	Si/Ti
$50SiO_2$–$50TiO_2$	–	1.5	1.6
$50SiO_2$–$50TiO_2$ t.t.	400	1.6	1.7
$50SiO_2$–$50TiO_2$ t.t.	600	1.8	1.9
$50SiO_2$–$50TiO_2$ t.t.	800	2.1	2.2
$50SiO_2$–$50TiO_2$ t.t.	1000	2.4	2.7
$70SiO_2$–$30TiO_2$	–	3.8	4.0
$70SiO_2$–$30TiO_2$ t.t.	1000	4.0	4.2
$90SiO_2$–$10TiO_2$	–	7.2	6.7
$90SiO_2$–$10TiO_2$ t.t.	1000	15.2	15.6

Conclusions

By means of the combined use of XPS-XAES, DTA-TG, XRD and SEM techniques, the microchemical structure of sol-gel SiO_2, TiO_2 and $x SiO_2$–$(1–x)TiO_2$ ceramics have been studied as a function of thermal treatments carried out up to 1200°C in air.

The proposed structure of the materials in as prepared conditions can be described as a composite between TiO_2 and SiO_2 moieties with a not negligible number of Si–O–Ti bonds that act also as crosslinking bonds between these units.

In the temperature range from 50 to 450°C, DTA-TG results evidence a remarkable mass loss due to the evaporation of organic solvents entrapped in the sol-gel materials and of the remnant organic components of the precursor metal alkoxides. Furthermore, with increasing temperature the arrangements between the units Ti–O–Ti–O–Ti and Si–O–Si–O–Si made by Si–O–Ti crosslinking bonds are broken thus inducing the formation of new Si–O and Ti–O bonds as well as a SiO_2 segregation phenomena.

The structure of these newly formed materials can be described as composed by a pure SiO_2 matrix and TiO_2 based particles crystallised in the quartz, anatase and rutile forms as a function of the chemical composition of the sol-gel materials and of temperature.

* * *

The authors thank C. Veroli for XRD analysis and the SEM laboratory of Roma II University where the characterisations have been performed by the authors.

References

1 C. J. Brinker and G. Scherer, ‘Sol-Gel Science, the Physics and Chemistry of Sol-Gel Processing’, Academic Press, San Diego 1989.
2 D. C. Bradley, R. C. Mehrotra and D. P. Gaul, ‘Metal Alkoxides’, Academic Press, New York 1978.
3 S. Dirè, F. Babonneau, C. Sanchez and J. Livage, J. Mater. Chem., 2 (1992) 239.
4 S. Dirè, L. Bois, F. Babonneau and G. Carturan, Polymer Preprints, 32 (1991) 501.
5 S. Dirè, J. Livage, F. Babonneau and G. Carturan, J. N. Cryst. Solids, 147-148 (1992) 62.
6 S. Dirè and F. Babonneau, J. Sol Gel Sci.Technol., 2 (1994) 139.
7 S. Dirè, R. Campostrini and R. Ceccato, Chemistry of Materials, 10 (1998) 268.
8 B. Zelinski and D. Ulhmann, J. Phys. Chem. Solids, 45 (1984) 1069.
9 Th. Gross, M. Ramm, H. Sonntag, W. Hunger, H. M. Weijers and E. H. Adem, Surf. Interf. Anal., 18 (1992) 59.
10 C. D. Wagner, L. H. Gale and R. H. Raymond, Anal. Chem., 51 (1979) 466.
11 C. D. Wagner and A. Joshi, J. Electr. Spectr. R. Phen., 47 (1988) 283.
12 P. C. Schultz, J. Am. Ceram. Soc., 59 (1976) 214.
13 E. Paparazzo, Surf. Interf. Anal., 12 (1988) 115.
14 E. Paparazzo, G. M. Ingo, G. Fierro and S. Sturlese, J. Am. Ceram. Soc., (Dec. 1988) 494.
15 E. Paparazzo, G. M. Ingo, G. Fierro and S. Sturlese, J. Vac. Sci. Technol. A, 7 (1989) 2496.
16 N. S. Gluck, H. Sankur, J. Heuer, J. DeNatale and W. G. Gunning, J. Appl. Phys., 69 (1991) 3037.