Journal of the European Ceramic Society **13** (1994) 73–80

Study of the Behaviour of Al_2TiO_5 Materials in Reducing Atmosphere by Spectroscopic Techniques

A. Durán, H. Wohlfromm* & P. Pena

Instituto de Cerámica y Vidrio (CSIC), 28500 Arganda del Rey, Madrid, Spain

(Received 11 February 1993; revised version received 12 July 1993; accepted 18 August 1993)

Abstract

The thermal stability of two materials based on aluminium titanate, obtained through reaction sintering at 1450°C and heat treated in atmosphere of N_2/H_2 90/10 was studied using spectroscopic techniques.

The samples were analysed by reflectance in visible, UV and NIR, electronic paramagnetic resonance (EPR) and Mössbauer spectroscopy. These techniques give coinciding results with regard to the reduction of Ti^{4+} to Ti^{3+} and to changes in the structural site changing of Fe^{3+} in reducing atmosphere.

Die thermische Stabilität zweier auf Aluminiumtitanat basierender Materialien wurde spektroskopisch untersucht. Ihre Herstellung erfolgte durch Sintern bei 1450°C und Wärmebehandlung in einer N_2/H_2 Atmosphäre der Zusammensetzung 90/10.

Die Charakterisierung der Proben erfolgte mittels ihres Reflektionsverhaltens im sichtbaren und UV Bereich, sowie durch NIR, Elektronen-Paramagnetische-Resonanz (EPR) und Mössbauer-Spektroskopie. Die verschiedenen Untersuchungsmethoden ergaben übereinstimmende Ergebnisse bezüglich der Reduktion von Ti^{4+} zu Ti^{3+} und der Änderung der Fe^{3+} Position in einer reduzierenden Atmosphäre.

On a étudié la stabilité thermique de deux matériaux à base de titanate d'aluminium, obtenus par frittage réactive à 1450°C, et ayant subi un traitement thermique sous atmosphère de N_2/H_2 90/10, au moyen de techniques spectroscopiques.

Les échantillons ont été étudiés par réflectance dans le domaine visible, UV, NIR, résonance paramagnétique électronique (EPR) et spectroscopie Mössbauer. Ces techniques donnent des résultats convergents aussi bien pour la réduction de Ti^{4+} en Ti^{3+} que pour le changement du site occupé par Fe^{3+} dans des conditions réductrices.

1 Introduction

The spectrometric technique of electronic paramagnetic resonance (EPR) is traditionally used in the study of states of oxidation and of the coordination of the transition metal ions in different materials, e.g. glass and monocrystals.

These ions are also active in visible and ultraviolet, since they have an incomplete ***d*** layer and consequently show electronic transitions between the levels of these ***d*** orbitals. The technique of diffuse reflectance, which can be applied to opaque or powdered samples, extends the type of materials which can be studied by absorption, and make it possible to analyse states of oxidation and the coordination of transition metals in ceramic materials whether they be sintered or in powder form.

Mössbauer spectroscopy is the most common and precise technique to determine states of oxidation and the coordination of iron in different materials.

The Ti^{3+} ion, which has an electronic structure $3d^1$, has been widely studied through EPR in glass, monocrystals and in mullite;[1-3] its characteristic resonance, with *g*-factor equal to 1.93–1.94, is always assigned to Ti^{3+} in octahedral coordination with varying degrees of distortion. This ion has also been characterized by visible and UV spectrophotometry; less efficiently than in EPR, trivalent titanium presents a wide band at around 600 nm, which can be split into three components at 450, 560 and 750 nm, which correspond to a charge exchange $Ti^{3+} \rightarrow Ti^{4+}$ and to the doublet produced by the Jahn–Teller effect of the trivalent titanium in a octahedral coordination, respectively.[2]

The Fe^{3+} ion has an electronic structure of $3d^5$ with a spherical charge distribution. This configuration is stable and shows no preference between octahedral or tetrahedral sites; its behaviour is only controlled by the size of the cations in the lattice. Thus, in mullite at high temperature, Fe^{3+} can replace Al_{IV}^{3+} or Al_{VI}^{3+}.

---

* Present address: BASF AG, ZAA/K, D-67056 Ludwigshafen, Germany.

Journal of the European Ceramic Society 0955-2219/94/$7.00

The incorporation of iron has been studied in different crystalline structures through spectrometric techniques in sillimanite, kaolinite, mullite and brucite.[4-6] Schneider & Rager made the most complete study, and, in their work on the incorporation of iron in mullite, distinguished three EPR signals corresponding to Fe^{3+} ions: a site I ($g = 6.8$ and 5.1) assigned to octahedral positions with axial symmetry, a centre II ($g = 4.2$) corresponding to highly crystalline sites which may correspond to a completely orthorhombic or tetrahedral crystalline field, and a centre III ($g = 2.0$) assigned to Fe^{3+} in more distorted octahedral positions or to clusters.

The electronic structure $3d^5$ of Fe^{3+} is the reason why this ion has the same number of bands with octahedral or tetrahedral coordination. However, as the difference in energy of an electron in different environments, Δ, is $\Delta_{tetr} = -4/9\ \Delta_{oct}$, the ion absorption bands in an octahedral field are further separated than in a tetrahedral field. Moreover, in the latter case the bands have a greater molar absorption factor.

Aluminium titanate Al_2TiO_5 is a synthetic ceramic material of potential interest for many structural applications, owing to its high melting point, low thermal conductivity and excellent thermal shock resistance. However, a critical feature, which greatly limits the mechanical properties of polycrystalline Al_2TiO_5, is considerable intergranular microcracking, which occurs due to the high thermal anisotropy of individual grains.

Another problem arises from the thermodynamical decomposition of aluminium titanate:

(a) in an oxidizing atmosphere—$pO_2 = 0.21$ atm—at temperatures of less than 1280°C, because of a eutectoid reaction in corundum (Al_2O_3) and rutile (TiO_2).[7] This can be avoided by replacing ions Al^{3+} or Al^{3+} and Ti^{4+} by small quantities of ions like Mg^{2+} and Fe^{3+}, which form solid solutions (ss)[8] of Al_2TiO_5, for which the temperature of the eutectoid could even be below 800°C; thus, the decomposition kinetics at lower temperatures than the eutectoid will be very slow and Al_2TiO_5 (ss) could be considered as being stable from an engineering point of view.[9]

(b) in a reducing atmosphere—according to the equilibrium diagram Al_2O_3–TiO_2–Ti_2O_3 the Al_2TiO_5 produces alumina mixtures and a pseudobrookite phase (Ps) which can be represented by the formula $Al_{(2-2x)}TiO_{(5-\frac{10}{3}x)}$[9-11] (see Appendix).

The influence of reducing atmospheres on the stability of solid aluminium titanate solutions and especially the effectiveness of the said cations in these atmospheres have not yet been established.

The purpose of this research has been the study of the influence of a reducing atmosphere on the stability of aluminium titanate materials which have been stabilized with iron and magnesium. The evolution of the oxidation state and the coordination of ions Ti^{3+}, Fe^{2+} and Fe^{3+} present in these materials can be studied on the basis of the EPR spectra and the diffuse reflectance in the visable UV spectra. The Mössbauer spectra confirm the information provided by the other techniques used.

2 Experimental

2.1 Preparation of materials

Two compound materials based on Al_2TiO_5, one stabilized with MgO (MAT90) and the other with Fe_2O_3 (BTC) were studied. The raw materials used were TiO_2 (Merck 808), alumina (Alcoa CT3000SG), zircon (Quiminsa Opazir S), Probus MgO and Surinam bauxite. The high iron content of this bauxite is used to stabilize the BTC material; however, in the MAT90 sample, 2% MgO was added for the same purpose, since zircon has a very low iron content ($\ll 1\%$). Both compounds were subjected to the same processing: mixing the raw materials by attrition milling, isostatic pressing at 200 MPa and sintering in an oxidizing atmosphere ($pO_2 = 0.21$ atm) at 1450°C for 2 h (MAT90 and BTC samples). Following this processing route an Al_2TiO_5 matrix reinforced with ZrO_2 and/or mullite particles is obtained through the reaction of $ZrSiO_4$ (or kaolin) with Al_2O_3 excess. These samples were later treated in a reducing atmosphere of N_2/H_2 90/10 at 975°C ($pO_2 \leq 10^{-20}$ atm) for 8 h (MAT90 R and BTC R samples). This treatment was chosen for studying the first stages of reaction in a temperature range useful for engineering applications.

Table 1 shows the physical and chemical characteristics of these materials.

2.2 Spectroscopic techniques

The EPR spectra were obtained with a Varian E-12 spectrometer which operates on microwave frequencies in the X band (9.5 GHz), on powdered samples at room temperature. Different scale factors, RG, were used to get better resolutions in the detected peaks.

In order to study the absorption behaviour a Perkin Elmer model Lambda 9 spectrophotometer was used on powdered samples. The diffuse reflectance spectra were obtained by using the integrating sphere of the same equipment.

Table 1. Physical and chemical characteristics of the materials

	MAT 90	*BTC*
Chemical analysis (wt%)		
Al_2O_3	47·20	57·18
TiO_2	40·20	38·21
ZrO_2	6·19	0·18
SiO_2	3·22	3·55
MgO	1·56	0·10
CaO	0·06	0·03
Fe_2O_3	0·03	0·90
Na_2O	0·09	0·08
K_2O	0·02	0·03
P_2O_5[a]	0·10	0·10
Ignition loss	1·10	1·88
Mineralogical analysis (vol.%)		
β-Aluminium titanate (ss)	90	90
Mullite (ss)	7	10
Monoclinic zirconia (ss)	3	—
Density (g/cm^3)	3·60	3·34
Bending strength (MPa)	45 ± 4	87 ± 4

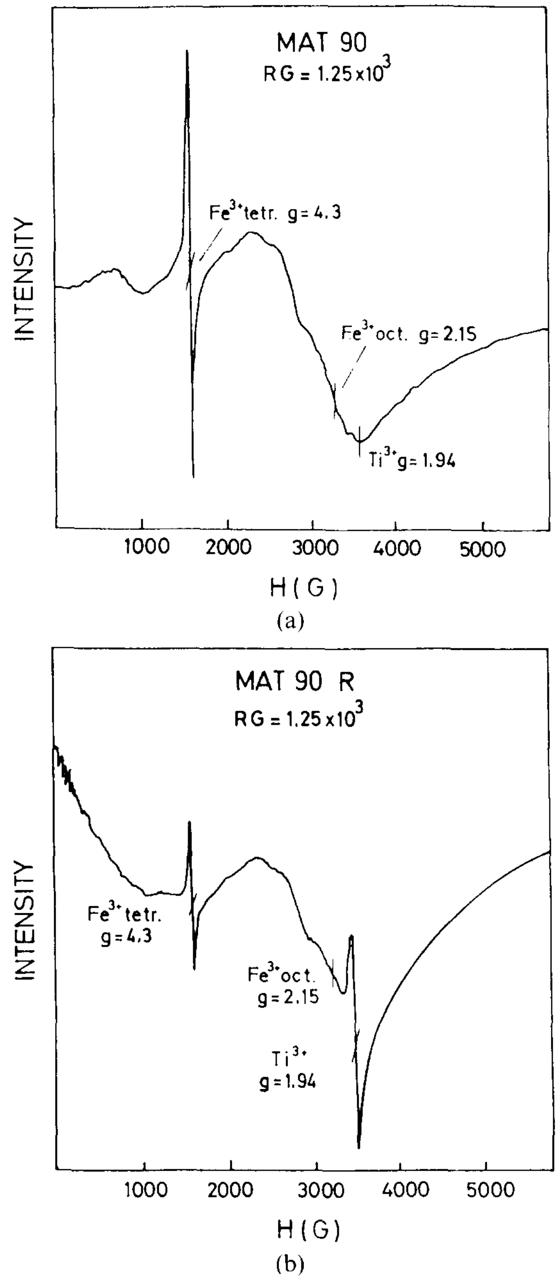
[a] Low precision.

The Mössbauer study was carried out on powdered samples at room temperature and at 15 K in a conventional constant acceleration spectrograph, with a source of ^{57}Co in an Rh matrix and with a closed circuit He cryostat. The experimental spectra were adjusted to a sum of Lawrentian curves through a calculus programme with the restriction of equal width (QG) and equal Lawrentian area for the two lines of each doublet. Layers of different thickness were tried and the spectra were finally made with ≈ 115 mg/cm^2 and accumulating approximately 3×10^6 and 7×10^6 computations per channel for the original sample and the sample which had been treated in a reducing atmosphere.

Results

In the specimens obtained after the thermal treatment at 975°C in reducing atmosphere, no significant variations were detected either with regard to density or to mineralogical (XRD) or microstructural analysis (RLM and SEM). The only notable change was the final colour of the samples; those containing MgO were bluish and those containing larger quantities of iron were yellowish. For this reason, alternative techniques for evaluating the changes which had taken place during the thermal treatment were looked for.

Figures 1–4 show the spectra of EPR and diffuse reflectance of the samples studied. In the EPR spectra of the samples MAT90 and MAT90 R (Fig. 1), Ti^{3+} is detected in octahedral coordination ($g = 1.94$). Moreover a large increase in Ti^{3+} concentration is detected by EPR and by visible-UV spectroscopy in the sample treated in reducing atmosphere (Figs 1(b) and 2).



(a)

(b)

Fig. 1. EPR spectra of MAT90 samples with different treatments. (a) Reaction sintered at 1450°C (MAT90). (b) Reaction sintered at 1450°C and treated in N_2/H_2 atmosphere at 975°C for 8 h (MAT90 R).

In the untreated BTC sample no peak corresponding to Ti^{3+} is detected by any of the techniques used (Fig. 3(a)); in the BTC R sample one cannot exclude the presence of small quantities of this ion, due to the fact that the characteristic resonances of Fe^{3+} in octahedral coordination (sites III) and of Ti^{3+} overlap (Fig. 3(b)).

Fe^{2+} is not detected in any of the spectra of the MAT90 sample (Figs 1 and 2). This ion has a very high efficiency in visible-UV spectra, and very small quantities may be detected from its characteristic band situated at around 1050 nm. However, the concentration of iron impurities in this composition, 0.03%, cannot be detected by visible-UV spectroscopy when the ion is in its oxidated form.

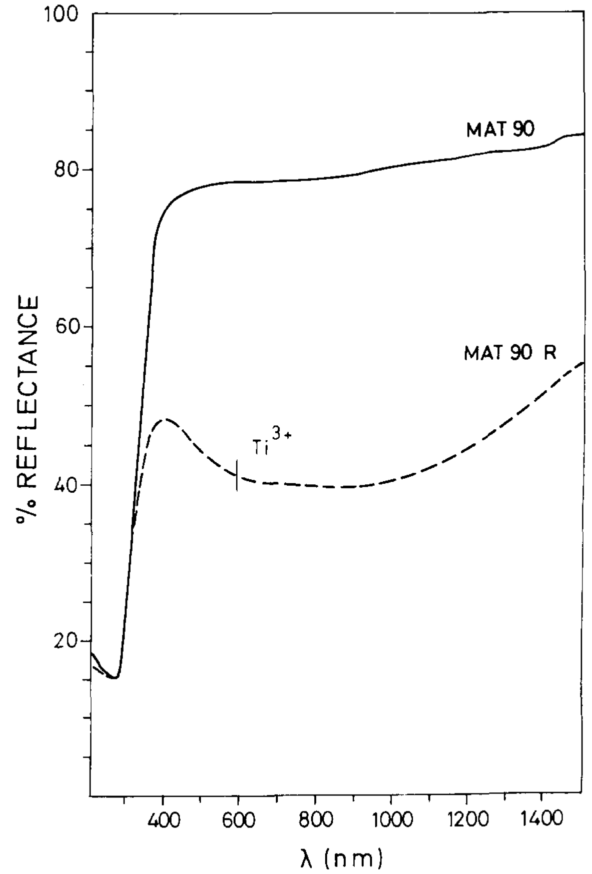


Fig. 2. Reflectance spectra of MAT90 samples with different treatments.

The EPR technique, which is very sensitive to Fe^{3+}, leaves one in no doubt that the iron which is in this state of oxidation is largely in centres of type II. Centres of type I (g = 6.8 and 5.1) and traces of centres III (g = 2.1) also appear (Fig. 1(a)).

The reducing process does not provoke the appearance of Fe^{2+}, as can be observed in the reflectance spectra. All of the iron present continues in its oxidated state, although part of it changes sites in the crystal lattice. On the other hand, the octahedral sites of type I disappear and those of type II decrease, giving way to a significant increase in type III octahedral sites.

In the original BTC sample iron is not observed in a reduced state by any of the techniques used. In this case Fe^{3+} can be detected both by EPR and by visible-UV spectroscopy since it is more highly concentrated, 0.90% Fe_2O_3 (Figs 3 and 4). The reflectance spectra in the original BTC sample, Fig. 4, show three bands situated at approximately 380, 460 and 640 nm which can be attributed to Fe^{3+} in tetrahedral coordination. Figure 3(a) presents a single very intense EPR band, located at g = 4.3, corresponding to type II sites; traces of trivalent iron can also be detected in type III octahedral coordination. In the BTC R sample Fe^{2+} is not detected, as in the previous samples. The reduction treatment causes a large decrease in oxidated iron in type II sites, associated with the appearance of a very intense EPR band of Fe^{3+} in octahedral sites of type III, g = 2.1, Fig. 3(b). This fact is confirmed through reflectance spectra, where the bands are further separated and less intense, which is related to the presence of a large part of Fe^{3+} in octahedral coordination (Fig. 4).

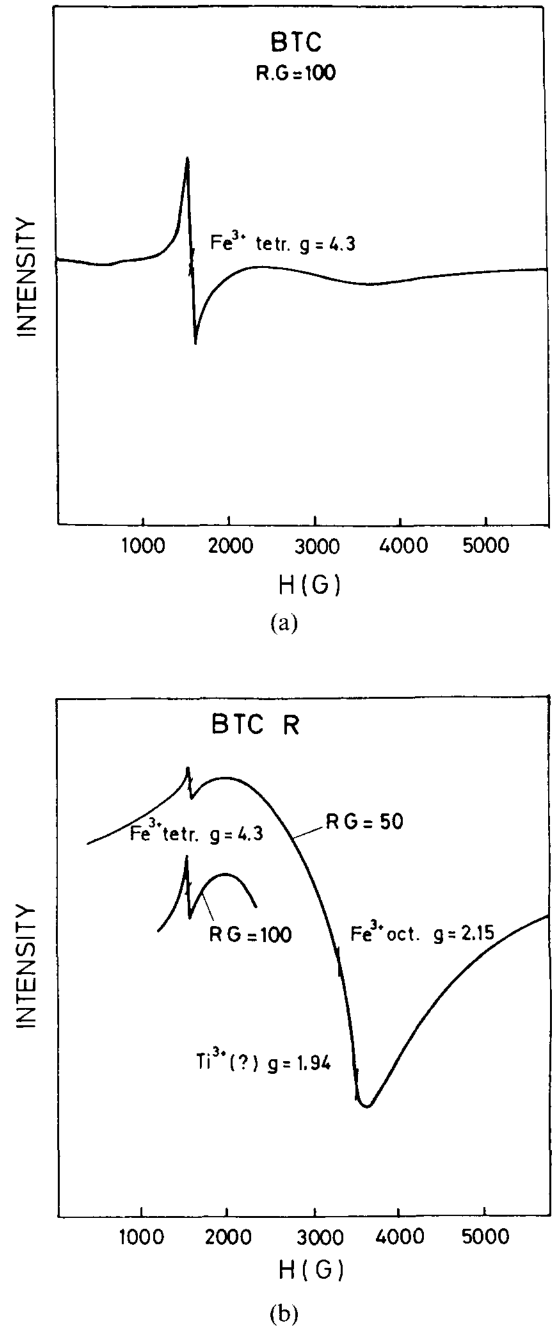


Fig. 3. EPR spectra of BTC samples with different treatments. (a) Reaction sintered at 1450°C (BTC). (b) Reaction sintered at 1450°C and treated in N_2/H_2 atmosphere at 975°C for 8 h (BTC R).

Moreover, the treatment does not have a strong effect on the state of oxidation of titanium. Ti^{3+} is not observed by spectrophotometry and the band of oxidized iron at g = 2.1 conceals the possible presence of this ion in the EPR spectrum.

The fact that Fe^{2+} was not detected in these samples, despite the reducing treatment, led the authors to confirm this through ^{57}Fe Mössbauer spectroscopy. However, the low Fe content and the high Ti content of the samples constitute big drawbacks to the study of these samples by this technique,[12] since the absorption of ^{57}Fe Mössbauer radiation (14.4 KeV) in Ti is four times as much as in Si. Because of this it was only possible to obtain spectra of the samples BTC and BTC R, those with a higher iron content.

Figure 5 shows the spectra of the BTC composition, original and treated, at room temperature and at 15 K. All of them present identical spectral morphology, characterized by a couple of peaks centred at ≈ 0.35 mm/s, typical of Fe^{3+}, which can be adjusted to a doublet. Given the composition of the sample, the spectral absorption obtained is very low and, consequently, so is the quality of the spectra, especially in the untreated sample. However, the results obtained indicate that in both samples the iron is largely in the form of Fe^{3+} and the presence of Fe^{2+} can be ruled out in the samples in larger quantities than 5% of the total of the types of iron present. Moreover, the absence of a magnetic component in spectra at 15 K confirms the paramagnetic nature of the ferric doublet. This makes it possible to rule out the presence of clusters of iron in the samples, so that the type III EPR centres can be assigned to Fe^{3+} in octahedral coordination.

Given the low quantity of iron and the interference of titanium, it is not possible to determine

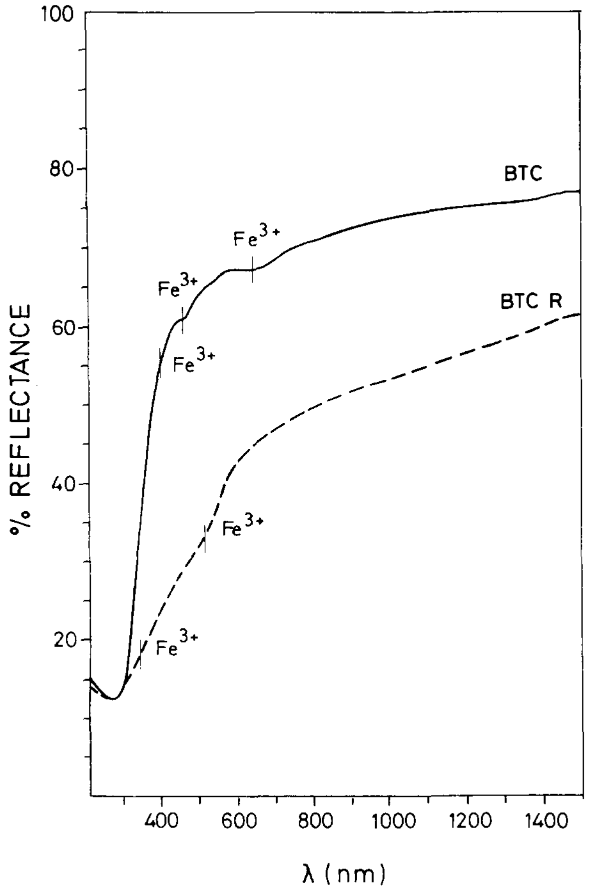


Fig. 4. Reflectance spectra of BTC samples with different treatments.

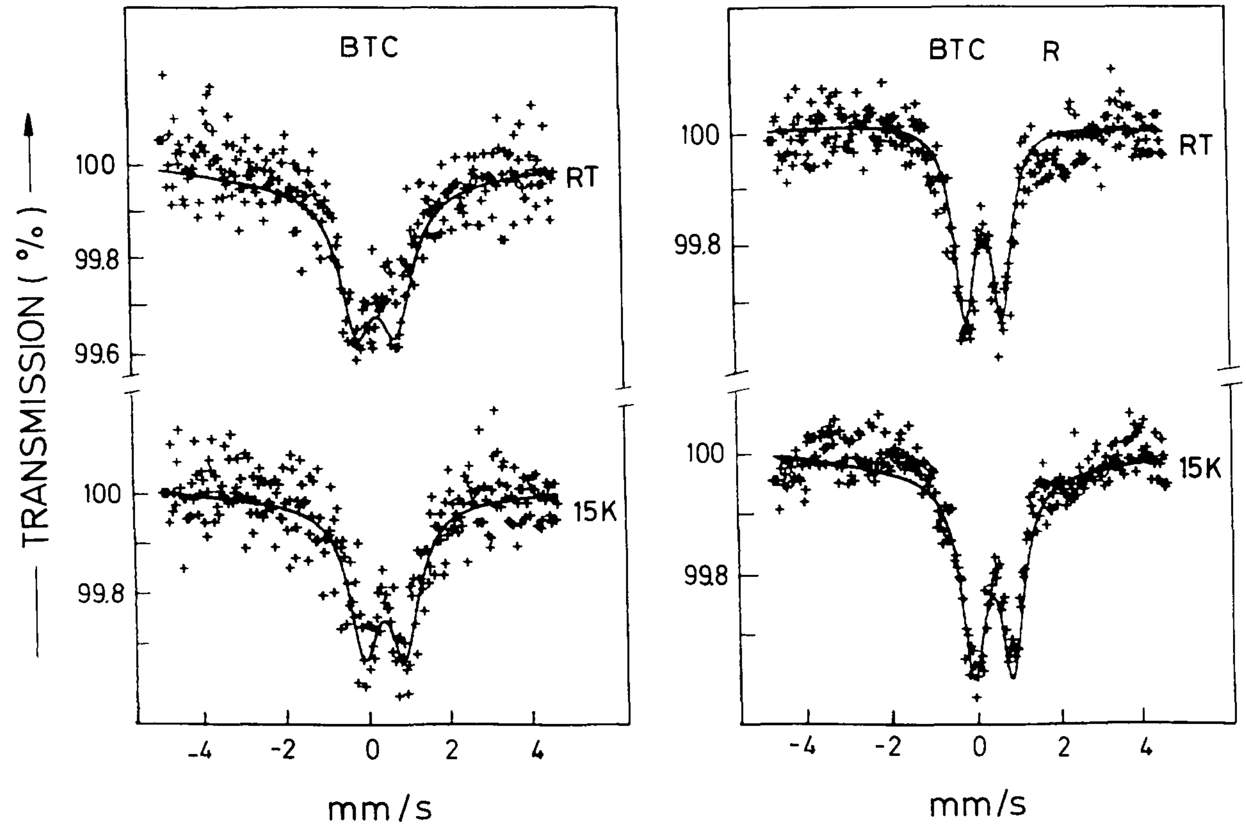


Fig. 5. Mössbauer spectra of BTC and BTC R samples at room temperature and 15 K.

Table 2. Iron and titanium ions in the studied samples

	MAT	*BTC*
As-fired	Fe^{3+} type II; traces types I and III; Ti^{3+}	Fe^{3+} type II; traces type III
Reducing atmosphere	Fe^{3+} types II and III; Ti^{3+} strong signal	Fe^{3+} type III (strong); type II; Ti^{3+} traces (?)

quantitatively the proportion of Fe^{3+} in its tetrahedral and octahedral forms, although both types are present in both samples. These results are presented in Table 2.

Discussion

The results obtained indicate a series of differences between the redox states and the coordination of the transition metal ions in the two samples, both in those sintered in air and after a treatment in reducing atmosphere.

The appearance of Ti^{3+} (g = 1.94) in the MAT90 sample sintered in air indicates that part of the Ti^{4+} was reduced to Ti^{3+}, even in an oxidizing atmosphere, replacing Al^{3+} in the titanate lattice. Freudenberg[10] already mentioned this possibility when he explains the non-stoichiometry of Al_2TiO_5 in samples sintered in oxygen because of the partial replacement of Al^{3+} by Ti^{3+}. In the BTC composition, however, Ti^{3+} is not detected in the original sample and traces of this ionic form only appear after the reducing treatment.

All the iron detected in the two compositions studied is always in the form of Fe^{3+}, even after treatment in a reducing atmosphere, which is surprising but borne out by the different techniques used in the experiment. This contradicts the general belief that iron cannot be used as a stabilizer of aluminium titanate in reducing atmospheres, since its reduction to its ferric state would provoke its exolution from the Al_2TiO_5 crystal lattice.[9]

The majority of ferric iron is found in both of the untreated samples in type II sites, and this effect is much more pronounced in the BTC composition. In aluminium titanate[13] the Fe^{3+} enters the lattice and replaces Al^{3+} in octahedral coordination and in mullite in octahedral and tetrahedral sites, although according to Schneider[3] the intensity of type I centres in mullite diminishes as the iron content increases in the presence of titanium. This confirms the existence of joint solid solutions of Ti^{4+} and Fe^{3+} in mullite where Ti^{4+} occupies octahedral sites and Fe^{3+} preferably tetrahedral sites.

The fact that the ferric ion changes lattice sites as a result of thermal treatment at 975^{0}C in a reducing atmosphere, can be explained by a variation in the iron content in the solid solution of the aluminium titanate and/or mullite. Since in Al_2TiO_5 coordinations are always octahedral, the disappearance of tetrahedral sites and the subsequent appearance of octahedral sites could be interpreted as a migration of Fe^{3+} from the mullite solid solution to Al_2TiO_5; the other possible coordination change, from tetrahedral to octahedral sites into mullite, is less probable according to Schneider[3] and Schneider and Rager.[5]

The difference between the BTC and MAT90 samples arises from the fact that in the case of the BTC sample with a higher iron content, not even treatment in N_2/H_2 atmosphere manages to reduce Ti^{4+} to Ti^{3+}. This means that the iron is acting as a stabilizer of the aluminium titanate lattice, thus preventing reduction of the titanium.

A feasible interpretation of the results observed is based on energy criteria. The orthorhombic structure of the aluminium titanate (*Cmcm*) is constituted by double chains of octahedrons (MeO_6) where the metallic ion can occupy two different sites of multiplicity 4 or 8. Experiments with both X-ray diffraction[14] and high resolution electronic microscopy[15] have proved that the Al^{3+} and Ti^{4+} ions occupy these sites at random. The thermal instability of Al_2TiO_5 at low temperatures is attributed to the distortion of the lattice produced as a result of the substantial difference between the ionic radii of Al^{3+} (0.50 Å) and Ti^{4+} (0.68 Å), which can be reduced by introducing medium-sized ions into the lattice.

The Al_2TiO_5 admits iron and titanium in a trivalent state in the solid solution replacing Al^{3+} (Ps_1), while in the case of the diatomic ions Mg^{2+} and Fe^{2+} two Al^{3+} ions are replaced by one Ti^{4+} ion and one Mg^{2+} or Fe^{2+} ion (Ps_2).[9]

The Fe^{3+} and the Ti^{3+} enter in the solid solution and replace Al^{3+} in octahedral positions. If the ionic radius is borne in mind (Ti^{3+}= 0.76Å and Fe^{3+}= 0.64Å) the Fe^{3+} solid solution will be more stable in terms of energy than that of Ti^{3+}. Consequently, if there is enough Fe^{3+}, reduction of titanium would not take place.

In the MAT90 samples, however, the quantity of iron is much lower, and from the beginning, Fe^{3+} exists in solid solution in the aluminium titanate (type III sites) and in mullite (sites I and II). As in the case of BTC, the reducing treatment causes the Fe^{3+} to migrate from the mullite to the aluminium titanate lattice, replacing Al^{3+} ions in octahedral coordination, but, given its low concentrations, Ti^{4+} is also reduced to Ti^{3+}, as can be seen by EPR and spectrophotometry; the exolution of Al_2O_3, however, is so limited that it has not been detected through X-ray analysis, although some alumina crystals can be seen through optic microscopy on the edges of the aluminium titanate grains.

Consequently, a large quantity of iron in solid solution helps to stabilize the pseudobrookite lattice. At the temperature of the experiment, 975°C, and in a reducing atmosphere, the iron acts as a redox buffer, preventing the reduction of Ti^{4+} to Ti^{3+}.

Conclusions

(i) The spectrometric techniques have shown their usefulness in detecting changes in valency and coordination in transition metal ions in aluminium titanate matrixes.

(ii) In the materials studied, no Fe^{2+} was detected, not even after reducing treatment.

(iii) In the case of Fe^{3+} a change in coordination sites with reducing treatment was detected by EPR and confirmed by visible-UV spectroscopy. This change could be interpreted as a migration from tetrahedral sites in mullite to octahedral sites in aluminium titanate.

(iv) The less iron in the samples the greater the reduction of the titanium. The appearance of large quantities of Ti^{3+} can mean the beginning of the decomposition of aluminium titanate, according to the reaction:

$$\begin{aligned}&Al_2TiO_5\ (ss)\\&\rightarrow Al_{(2-2x)}Ti^{4+}{}_{(1+\frac{2}{3}x)}Ti^{3+}{}_{(\frac{2}{3}x)}O_{(5-\frac{10}{3}x)}\\&\quad + Al_2O_3 + x/6O_2\end{aligned}$$

although this needs to be confirmed through more prolonged reducing treatments.

Acknowledgements

The authors would like to thank Dr M. Gracia García for the Mössbauer analysis, Dr J. García Solé for the EPR spectra and Dr C. Pascual for her collaboration in the discussion of this work, which has been subsidized by the CICYT Projects MAT88-0156 and MAT89-727.

References

1. Yafaev, N. R. & Yablokov, Y. V., *Soviet Phys. Solid State*, **4** (1962) 1123.
2. Bausá, L., García Solé, J., Fdez. Navarro, J. M. & Durán, A., *J.Non-Cryst.Solids*, **127** (1991) 267–72.
3. Schneider, H., In *Ceramic Transactions*, Vol.6, Mullite and Mullite Matrix Composites, ed. S. Somiya, R. F. Davis & J. A. Pask, 1990, pp. 135–56.
4. Le Marshall, J., Hutton, D. R., Troup, G. J. & Thyer, J. R. W., *Phys. Stat. Sol. (a)*, **5** (1971) 769–73.
5. Schneider, H. & Rager, H., *Ceramics International*, **12** (1986) 117–25.
6. Mestdagh, M. M., Vielvoye, L. & Herbillon, A. J, *Clay Minerals*, **15** (1980) 1–13.
7. Kato, E., Daimon, K. & Takahashi, J., *J. Am. Ceram Soc.*, **63** (1980) 355–6.
8. Ishitsuka, M., Sato, T., Endo, T. & Shimada, M., *J. Am. Ceram Soc.*, **70** (1987) 69–71.
9. Woerman, E., Thermal stability of pseudobrookite solid solutions. DFG-Final Report, personal communication, 1985.
10. Freudenberg, B., PhD Thesis, Ecôle Polytêchnique, Lausanne, 1987.
11. Hennicke, H. W. & Lingenberg, W., The formation and decomposition of aluminium titanate. II. The decomposition reaction of aluminium titanate. *cfi/Ber.DKG*, **63** (1986) 100–6.
12. Birks, L. S. & Criss, J., In *Handbook of Spectroscopy*, Vol.III, ed. J.W.Robinson. CDC Press Inc., Florida, 1981, pp. 8–9.
13. Bayer., G., *J. Less-Common Metals*, **24** (1971) 129–38.
14. Morosin, B. & Lynch, R. W., *Acta Cryst.* **B28** (1972) 1040–6.
15. Epicier, T., Thomas, G., Wohlfromm, H. & Moya, J. S., *J.Mat.Res.* **6** (1991) 138–45.

Appendix

The appearance of large quantities of Ti^{3+} detected by visable-UV spectroscopy and of Al_2O_3 in the Al_2TiO_5 indicates that aluminium titanate in a reducing atmosphere decomposes according to a chemical reaction which can be explained in three stages:

1. Presence of Schottki type defects, Al^{3+} and O^{2-} vacancies:

$$\text{Lattice} \rightarrow xAl_2O_3 + 2xV'''_{Al} + 3x\ V''_O$$

2. Migration of Ti^{4+} from Ti positions to Al positions.

$$Ti_{Ti} + V'''_{Al} \rightarrow Ti^{\cdot}_{Al} + V''''_{Ti}$$

3. Reduction of the Ti^{4+} to Ti^{3+} and charge compensation through the creation of oxygen vacancies

$$2Ti^{\cdot}_{Al} \rightarrow 2Ti_{Al} + 2e'$$

$$O_O + 2e' \rightarrow V''_O + (1/2)\ O_2$$

$$2Ti^{\cdot}_{Al} + O_O \rightarrow 2Ti_{Al} + (1/2)\ O_2 + V''_O$$

After duly adjusting the vacancies and the charges the complete reaction can be written as follows:

$$\begin{aligned}Al_2\,TiO_5 \rightarrow {}&[Al_{Al(2-2x)}\,Ti_{Ti(1-\frac{2}{3}x)}\,Ti_{Al(\frac{2}{3}x)}\,O_{O(5-\frac{10}{3}x)}\\&- V''_{O(\frac{10}{3}x)} + V'''_{Al(\frac{4}{3}x)}\,V''''_{Ti(\frac{2}{3}x)}]\\&+ xAl_2\,O_3 + x/_6\,O_2\end{aligned}$$

The degree of decomposition and of reduction of the titanium depends on the temperature and on the partial pressure of oxygen, but the phases obtained even in the extreme case of the reaction $x=1$ will be a mixture of the stoichiometrical proportions of the pseudobrookite phase Ti_3O_5 and Al_2O_3:

$$3\ Al_2TiO_5 \rightarrow 3Al_2O_3 + Ti_3O_5 + 1/2O_2$$

These results are in accordance with the equilibrium diagram Al_2O_3–TiO_2–Ti_2O_3, where there is a continuous solid solution between Al_2TiO_5 and Ti_3O_5, in addition to the fact that as the partial oxygen pressure decreases, the composition will move from that corresponding to the Al_2TiO_5 towards the Al_2O_3–Ti_2O_3 line. This area of the diagram corresponds to an area of biphase compatibility where pseudobrookite and Al_2O_3 coexist in a wide range of oxygen partial pressures (so that at high oxygen partial pressures, $x \approx 0$, the pseudobrookite will practically be Al_2TiO_5 and at low partial oxygen pressures, $x \approx 1$, the solid solution will practically be Ti_3O_5).