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Ageing Influence on Residual Carbon Content in Different Grain-Sized BaTiO$_3$ Ceramics Analysed by ^{12}C(d,p)^{13}C Nuclear Method

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Abstract

The residual carbon content in BaTiO$_3$ ceramics synthesized by the citric resin route has been determined by ^{12}C(d,p)^{13}C nuclear reaction technique. The C content inside ceramics depends on sintering conditions (heating rate, final temperature), and grain size. The deposition of carbon from the atmosphere as a function of time at the surface and in the subsurface layer of different ceramics exposed to air or to ultra-high vacuum was investigated. © 1997 Elsevier Science Limited.

Résumé

Le taux de carbone résiduel dans des céramiques de BaTiO$_3$ synthétisées par la voie 'résine citriques' a été évalué par une méthode nucléaire basée sur la réaction ^{12}C(d,p)^{13}C. Nous avons montré que le taux de carbone résiduel de ces céramiques dépend des conditions de frittage (rampe de température, température finale) et de la taille des grains. Nous avons étudié l'évolution en fonction du temps du taux de carbone à la surface ainsi que dans la sous-surface pour différentes céramiques exposées à l'air ou sous ultra-vide.

1 Introduction

The quantitative determination and chemical state of residual carbon are of importance in various areas of material science. The modes of synthesis recently developed using organic precursors in order to obtain more homogeneous materials may lead to the existence of residual carbon in the materials, even after the sintering step. Experiments have shown that carbon is present in a great number of minerals, metals or synthesized oxide single crystals with contents ranging from ten or so to several hundred ppm.[1-4] But very little has been published on ceramic samples.[5]

The main problem is the contamination of surfaces by atmospheric carbon and carbonaceous compounds in such a way that it is sometimes difficult to know if the carbon detected at the surface of a material originates in contamination or in diffusion from the bulk.[3]

Ceramics with a grain size of about 100 μm, sintered at 1400°C were studied in a previous paper.[6] We showed:

(i) that all attempts to clean the surface samples were unsuccessful;

(ii) that in the surface layer of ceramics ($\approx$ 0·4 μm) two types of carbon exist: i.e. surface adsorbed carbon that is easily desorbed under UHV conditions and material intrinsic carbon;

(iii) that there was a gradient of concentration from the surface (about 400 μg/g) to the bulk in which the carbon content was roughly evaluated at about 50 μg/g;

(iv) that the carbon contents depend on the ceramic shapes for the same sintering cycle: residual carbon present in the powder diffuses during the sintering step from the bulk to the surface of the ceramic and thus if the exchange surface with the atmosphere decreases, diffusion is slower and carbon contents increase.

The present study deals with the carbon content in BaTiO$_3$ ceramics sintered under different conditions with respect to final temperature and heating rate. The accumulation and mobility of C in dependence on time was determined by nuclear ^{12}C(d,p)^{13}C reaction.

2 Experimental

2.1 Samples

$BaTiO_3$ powders were obtained by a citric resin method, described in previous papers.[7,8] The mixed citrate $BaTi(C_6H_6O_7).3H_2O$, firstly prepared, was dissolved in a citric acid, ethylene glycol and water mixture in such a way that the ratio R = $BaTiO_3$ mass/solution mass was 1%. This mixture was fired at 700°C in static air to give pure $BaTiO_3$ powders after 2 h. A careful ultrasonic deagglomeration step was necessary[9] before isostatic pressing of powders into pellets at 250 MPa. The green compacts were sintered in air at different temperatures up to 1400°C using various heating rates. Our previous studies[7,8,10] showed that the best sintering conditions to obtain dense ceramics with fine grain size (about 1 μm) was a final temperature of 1230°C with a slow heating rate (4°C/h) between 1000 and 1230°C (see Table 1). To minimize the sintering time it is possible to increase the final temperature up to 1300°C and also the heating rate (Table 1). In order to study the grain size influence we also sintered samples at a higher temperature (1400°C) with two different heating rates. In Table 1 are reported the different sintering conditions and the ceramic characteristics: i.e. grain sizes estimated by scanning electron microscopy and density determined by geometrical measurement.[9] All ceramics exhibited the same shape (Ø ≈ 1 cm, e ≈ 2·4 mm).

2.2 Determination of carbon

$^{12}C(d,p)^{13}C$ nuclear technique using the deuterons from the Van-de-Graaff accelerator of the C.E.R.I was carried out. The method has been described in different articles.[1-3,6] The samples were quickly analysed after the sintering process in order to minimize the atmospheric contamination.

The measurement parameters were improved, compared with those used in our previous paper,[6] in order to guarantee reproducible conditions in recording the proton spectra.

The measurements were performed at 950 keV in an UHV chamber with a residual pressure of about 10^{-9} mbar obtained by a cryogenic pumping system; the detector was 64 mm from the sample position and the detection angle θ was 150°. A 10 μm Al foil was placed in front of the detector to stop scattered deuterons. A collimator 3 mm in diameter was placed in front of the UHV chamber in order to have a homogeneous beam. The beam current was about 10 nA. The counting time was about 45 min per data point. These conditions give a relatively low current density (1·56 nA/mm^2) and minimize both the heating effects of the beam and contamination by the carbon present in the UHV chamber.[11] The results given were averaged over approximately ten measurements.

For 950 keV energy incident deuterons, the t in g/cm^2 carbon content is given by the formula:

$$t = \frac{dA}{\Phi} \times \frac{1}{\frac{d\sigma}{d\Omega}} \times \frac{1}{d\Omega} \times \frac{M}{N}$$

dA = number of detected particles = reaction peak area

Φ = number of incident particles = $Q/1·6·10^{-19}$ with Q = total incident charge measured by integrator (C)

$d\sigma/d\Omega$ = differential cross-section (cm^2sr^{-1})

$d\Omega$ = solid angle determined by the detector and the impact point of the beam on the target (sr).

M = atomic mass of the studied nucleus ($g\ mol^{-1}$)

N = Avogadro's number.

The differential cross-section has been taken equal to 30 mbarns according to Ref. 12. The solid angle is $7·32 \times 10^{-2}$ in the UHV chamber.

Table 1. Characteristics of the studied ceramics:sintering conditions for different final temperatures, average grain size and density in d_{th} per cent (d_{th} = theoretical density)

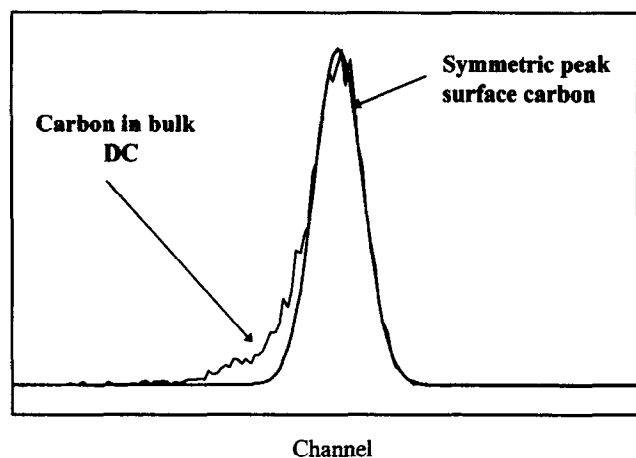| Final sintering temperature (°C)	Sintering rates	Total sintering time (h)	Grain size (μm)	% d_{th}
1230	20–700°C at 350°C h⁻¹ 700-1000°C at 50°C h⁻¹ 1000-1230°C at 4°C h⁻¹	65·5	1·6	96
1300	20–700°C at 350°C h⁻¹ 700-1300°C at 200°C h⁻¹	5	0·7	94·5
1400	20–600°C at 300°C h⁻¹ 600-1400°C at 70°C h⁻¹ 1400°C during 2 h	15·3	100	~99
1400 (slow)	20–700°C at 350°C h⁻¹ 700-1000°C at 50°C h⁻¹ 1000-1400°C at 4°C h⁻¹	108	~100 μm + 3 μm	95·5

Fig. 1. An experimental proton spectrum obtained from $^{12}C(d,p)^{13}C$ reaction in a BaTiO₃ ceramic with 950 keV deutrons.

Taking into account the density of ceramics and the resolution of the detector system the surface peak corresponds to a 0·4 μm thick layer. Thus it is possible to roughly estimate the carbon content in μg/g in this surface layer. An experimental proton spectrum of a BaTiO₃ ceramic containing C in the bulk with a C-rich surface layer is given in Fig 1. Thus the shape of the peak may give information about the C content in the surface layer and in the sub-surface zone. This peak may be decomposed into two contributions:

—a symmetric peak: the area of this peak corresponds to the C content in the surface layer of 0·4 μm.

—an asymmetric contribution on the left part of the peak: the area of this contribution, called DC, can be calculated by subtracting the area of the symmetric contribution from the total area of the peak. DC%, (a parameter defined as (DC area/total area) ratio) gives information on the carbon contents in the subsurface zone (deeper than 0·4 μm).

Considering the surface state of the materials and the statistical errors made in the measurements, one can estimate that the carbon concentrations in the surface layer are accurate to within 10%.[6]

3 Results and Discussion

In the first part of the study, we have determined the carbon contents in and under the 0·4 μm surface layer of ceramics sintered under different conditions summarized in Table 1.

The values of the total carbon content as well as those of DC% obtained with 950 keV energy incident deuterons are reported in Table 2.

The surface layers of ceramics sintered at 1230°C and 1300°C contain carbon contents of 380

Table 2. Carbon contents in the surface layer in ng/cm² and in μg/g and DC% parameter (see text) for the different sintering cycles

Final sintering temperature (°C)	1230	1300	1400	1400 (slow)
C contents (ng/cm²)	95	130	100	70
C contents (μg/g)	380	520	400	280
DC%	17	15·7	15·5	16

and 520 μg/g, respectively. Among the different parameters (grain size and sintering conditions), it appears that the total sintering cycle time: 65·5 h for the 1230°C sintering and 5 h for the 1300°C sintering, noticeably influences the carbon contents. For a final sintering temperature of 1400°C, the same phenomenon is observed between a short and a long sintering cycle. The carbon content decreases when the sintering time increases.

If we compare the carbon contents in two ceramics with a very different grain size but fabricated with short sintering cycles, for example 1300°C cycle with 0·7 μm grain size and 1400°C cycle with 100 μm grain size, it appears that the smaller the grain size the greater the carbon content (520 μg/g for 0·7 μm grain size and 400 μg/g for 100 μm grain size).

For all samples, the DC% value is almost the same; this means that ceramics exhibit a very small amount of carbon under the surface layer of 0·4 μm independently of the sintering conditions.

In a second part of this work, the change of the carbon contents was followed with time and storage conditions (in air or UHV).

The increase of carbon contents versus time of exposure to the air was first studied. Results are reported in Table 3 and in Fig. 2. Three types of behaviour are clearly observed:

(i) The carbon content in ceramics with small grain size increases very quickly during the first three weeks from 380 up to 905 μg/g in ceramics sintered at 1230°C and from 520 up to 780 μg/g in ceramics sintered at 1300°C.

(ii) The carbon content in large grain size ceramics (100 μm, sintered at 1400°C rapid heating) does not vary during the first three weeks and then increases linearly versus time.

(iii) The change of the carbon content in ceramics sintered at 1400°C with a slow heating cycle and exhibiting a bimodal grain size distribution (100 and 3 μm) follows the behaviour of large grain size ceramics during the first four weeks then that of small grain size ceramics after eight weeks.
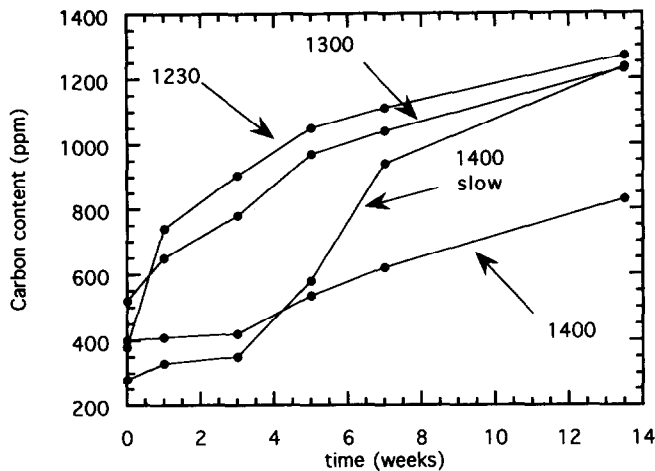
Fig. 2. C content versus time of exposure in ceramics sintered at different temperatures (see Table 3).

After 13·5 weeks all ceramics exhibit a carbon content of about 1300 μg/g except for the ceramics with a large grain size for which the carbon content is only 800 μg/g. The increase in carbon contents is greater in small grain size ceramics which can be explained by a segregation of carbon in the grain boundaries.

Figure 3 shows normalized proton spectra of (d,p) reaction performed at 950 keV on a 1400°C sintered ceramic immediately after the sintering step and after several weeks. The asymmetrical contribution of the peak (DC%) decreases with increasing total carbon content and, after 13·5 weeks, practically disappears. The same behaviour is observed for the three other ceramics. The change of the carbon concentration in the subsurface

Table 3. Evolution of carbon content μg/g versus time of exposure to the air for the different ceramics

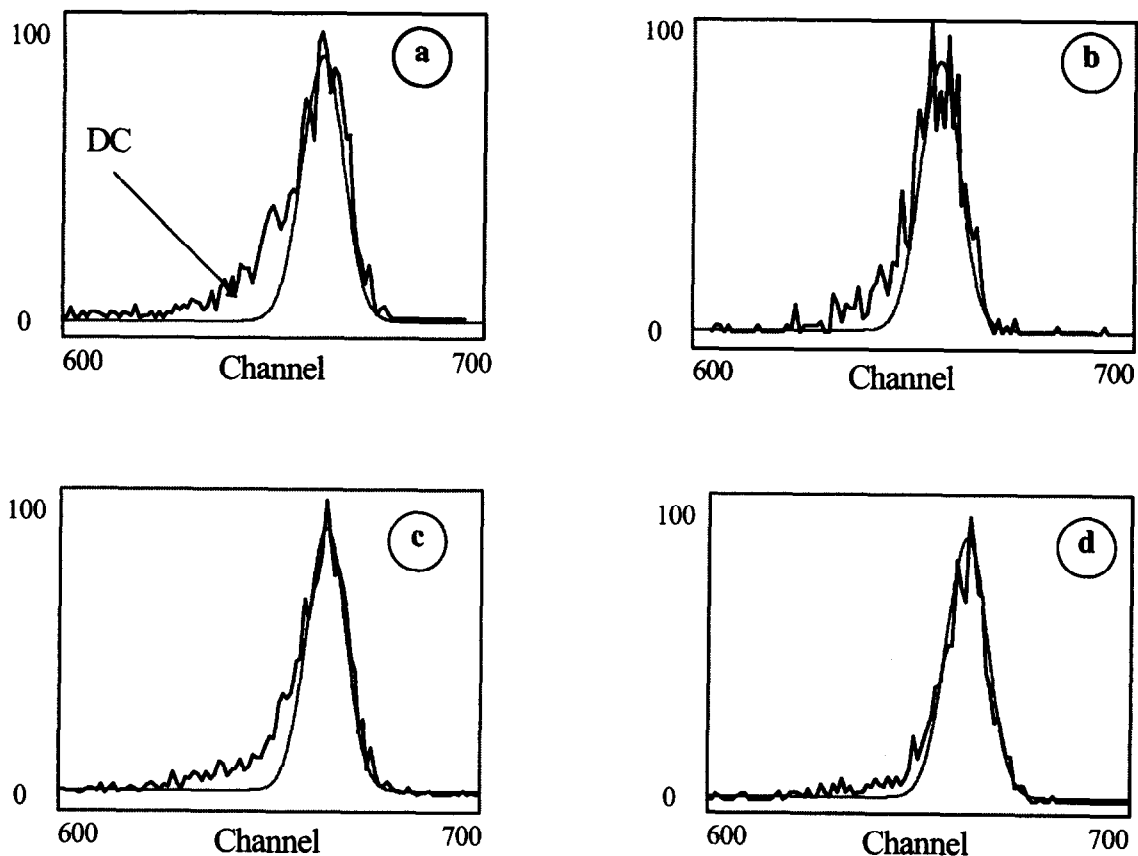| Final sintering temperature		0	1	3	5	7	13·5
		*Time in weeks*					
1230°C	C contents	380	740	905	1050	1110	1270
	DC%	17	5	4	2	2	2
1300°C	C contents	520	650	780	970	1040	1230
	DC%	15·7	5	1	0·7	0·5	0·5
1400°C	C contents	400	410	420	535	620	830
	DC%	15·5	15	15	7·7	3	1·5
1400°C (slow)	C contents	280	330	350	580	940	1235
	DC%	16	15	14	7	0·5	0·5

Fig. 3. Normalized proton spectra from ^{12}C(d,p)^{13}C reaction in BaTiO₃ sintered at 1400°C with a 950 keV deuterons, (a) just after the thermal treatment (b) after 2 weeks, (c) after 5 weeks, (d) after 13·5 weeks.

Table 4. Total carbon content and DC% parameter (see text) in two samples sintered at 1230°C, exposed to air or in UHV

Conditions of exposure (weeks)	Carbon content ($\mu g/g$)	DC%
Sample 1		
0	380	16
3 in air	905	4
5 in air	1050	4
5 in air + 4 in UHV	2290	17
Sample 2		
0	380	16
3 in air	905	4
3 in air + 2 in UHV	2880	21
3 in air + 2 in UHV + 4 in air	2960	15

zone does not follow that observed in the surface layer. Carbon accumulated as a function of time is preferentially located at the surface and comes mainly from the atmosphere.

This experiment shows clearly the role of grain size on the growth of surface carbon and the part played by atmospheric contamination.

Also we followed the change of the carbon content in two samples versus time of storage in a UHV chamber. The ceramics studied were sintered at 1230°C and showed a grain size of about 1·6 μm. Results are reported in Table 4.

Sample 1 was stored five weeks in the air. Its carbon content increased from 380 μg/g up to 1050 μg/g. It was then put in the UHV chamber for four weeks: its carbon content strongly increased and reached about 2300 μg/g. The same results were obtained with sample 2: after three weeks in the air and two weeks in UHV, its carbon content was about three times that of sample 1 exposed only to the air for five weeks. After exposing sample 2 again in air, the carbon content did not show a significant evolution. Figure 4 displays the typical proton spectra of samples before and after being stored in the UHV chamber. An increase in the peak asymmetry is observed: DC%

parameters of about 4% just before introduction into the UHV chamber reached 20%. There is an increase in carbon content in both the surface layer and subsurface zone certainly due to a diffusion of carbon from the bulk towards the ceramic surface. The intrinsic residual carbon of the material thus exhibits a high mobility.

Our results are in good agreement with those published by Freund and his coworkers about carbon in mineral single crystals[13–16] showing:

(i) the existence of a carbon content gradient between the bulk and the surface. According to Freund *et al.*, carbon atomically dissolved in MgO and olivine exhibits a tendency to segregate into a 0·5–1 μm thick surface zone. At low temperature, the carbon of the crystal bulk depletes and enriches in the surface layer by a factor of 100–1000 or more.

(ii) the high mobility of carbon: when heating a MgO or an olivine single crystal, Freund *et al.* observed a decrease in the carbon content in the subsurface zone. These authors conclude that carbon atoms diffuse back into the bulk. In UHV conditions we observed the reverse process.

4 Conclusions

The results obtained in this work may be summarized as follows:

—The residual carbon contents in the 0·4 μm surface layer of BaTiO₃ ceramics prepared by the citric route are found to vary between 280 μg/g and 520 μg/g depending on the sintering conditions and especially the heating time.

—After the sintering step the carbon content in the surface layer increases versus time. As this increase is more important in small grain size ceramics, carbon could be partly located in the grain boundaries.
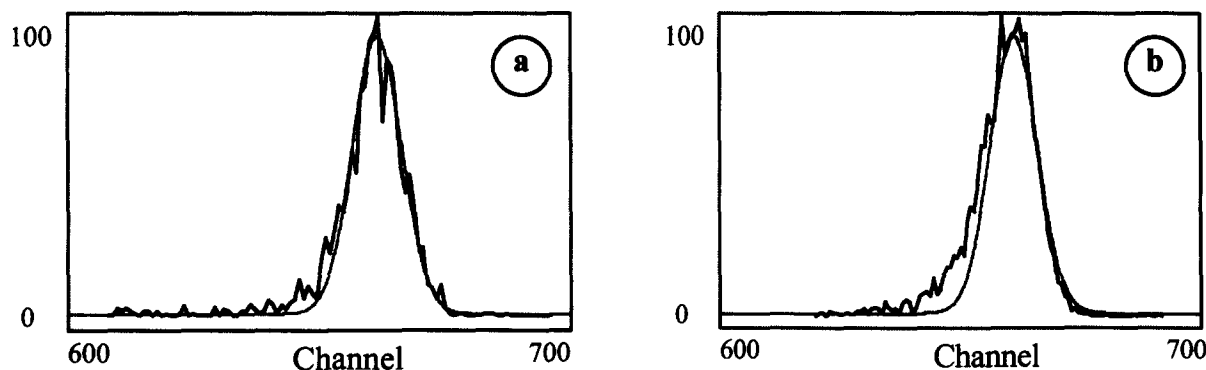

Fig. 4. Proton spectrum obtained from ¹²C(d,p)¹³C reaction in a sintered BaTiO₃ ceramic (1230°C) with 950 keV deuterons, (a) after three weeks exposure to air (b) after another two weeks in UHV.

—The values of the DC% parameters show that the relative carbon concentration in the subsurface decreases or increases versus time according to whether samples are stored in the air or in UHV. It can be concluded that:

(i) in air the detected enrichment in surface carbon comes essentially from the atmospheric contamination;

(ii) under UHV conditions, the carbon content detected is due to the carbon diffusion from the bulk to the surface.

XPS spectroscopy studies, now in progress, will allow to characterize the chemical state of carbon.

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