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Residual Carbon Detection in Barium Titanate Ceramics by Nuclear Reaction Technique

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Abstract

Residual carbon content in $BaTiO_3$ ceramics synthesized by the citric resin route has been evaluated by the ${}^{12}C(d,p){}^{13}C$ nuclear reaction technique. The C content inside ceramics sintered at 1400°C is about 50 ppm in weight. The surface layer (0·4 μm) exhibits a concentration of several hundreds or thousands ppm with two origins for the detected carbon: atmospheric contamination carbon adsorbed at the surface, which has been roughly evaluated, and material intrinsic carbon: its concentration depends mainly on the sintering conditions, shape of ceramic pieces and sintering temperature.

Der Kohlenstoffrestgehalt in $BaTiO_3$-Keramiken, hergestellt mittels der Zitrusharzmethode, wurde mit Hilfe der ${}^{12}C(d,p){}^{13}C$ Nuklearreaktionstechnik untersucht. Der C-Gehalt im Inneren der Keramiken, die bei 1400°C gesintert wurden, betrug 50 ppm Gew. Die Oberflächenschicht (0·4 μm) zeigt eine Konzentration von mehreren hundert oder tausend ppm, wobei der festgestellte Kohlenstoff aus zwei Quellen stammt: atmosphärische Kontamination durch adsorbierten Kohlenstoff, dessen Konzentrationsbeitrag ungefähr bestimmt wurde und Kohlenstoff, der aus der Probe stammt. Die Konzentration des Kohlenstoffs aus den Proben hängt hauptsächlich von den Sinterbedingungen, wie Form der Keramikteile und Sintertemperatur, ab.

Le taux de carbone résiduel dans des céramiques de $BaTiO_3$ synthétisées par la voie 'résines citriques' a été évalué par la réaction nucléaire ${}^{12}C(d,p){}^{13}C$. Le taux de carbone à l'intérieur des céramiques frittées à 1400°C est d'environ 50 ppm en masse. La couche de surface (0·4 μm) présente une concentration de quelques centaines ou millers de ppm avec une double origine pour le carbone détecté: le carbone de contamination adsorbé à la surface qui a pu être évalué et le carbone intrinsèque au matériau dont la concentration est principalement liée aux conditions de frittage, forme des pieces céramiques et température de frittage.

1 Introduction

Quantitative determination of carbon and its distribution 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. The same problem occurs when the fabrication includes the use of organic binders. The residual carbon remaining in the sintered samples may influence their properties. Work has shown that carbon is present in a great number of minerals, metals or synthesized single crystals with concentrations of from several tens to several hundreds of ppm,[1–4] but very little has been published on ceramic samples.[5]

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

The authors have undertaken a study on the detection of carbon in barium titanate ceramics obtained by the citric process[6,7] in order:

(i) To determine the carbon content in the surface layer and in the bulk;
(ii) To study the evolution of the carbon content as a function of different para-

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meters such as ceramic history (thermal treatment, granulometry, etc.) in-situ heating, laser ablation, etc.

(iii) To establish correlations between the carbon content and the properties of the ceramics, particularly the dielectric loss factor and the aging behaviour.

There are few techniques able to detect residual carbon at ppm levels. The Rosemount carbon analyser, consisting of heating a weighed sample in flowing O_2 to 1800°C and analysing the CO_2 evolved by an IR detector, gave very dispersed values of carbon concentrations and thus seems not precise enough in the present case. Techniques such as laser microprobe mass analyser (LAMMA),[8] X-ray induced photoelectron spectroscopy (XPS)[2] and nuclear reactions seem to be more adapted.

The first step of this work, in which $BaTiO_3$ ceramics sintered at 1300 and 1400°C have been studied by nuclear $^{12}C(d,p)^{13}C$ reaction, is presented here.

2 Experimental

2.1 Sample

$BaTiO_3$ powders were obtained by a citric resin method, described in previous papers.[6,7] The mixed citrate $BaTi(C_6H_6O_7)3H_2O$ is firstly prepared. Then it is 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 calcined at 700°C in static air and gives pure $BaTiO_3$ powders after 2 h. After an ultrasonic deagglomeration step, powders were pressed to give cylinders or discs; then they were sintered in air at 1400 or 1300°C for 2 h. The densities of the ceramics with an average grain size of 100μm approach 99% of the theoretical density (d_{th} = 6·02 g cm^{-3}) with a heating rate of 300° h^{-1} up to 600°C, then 70° h^{-1} up to final temperature.

2.2 Carbon analysis

The determination of carbon was carried out by $^{12}C(d,p)^{13}C$ nuclear technique using deuterons from the Van-de-Graaff accelerator of CERI. The method has been described in different articles.[1-3] Incident deuterons of energy $E°$ lose energy as they penetrate the target. Protons generated at positions 1,2,3 at increasing depths inside the target have initial energies $E°_1$, $E°_2$, $E°_3$; they lose energy in amounts proportional to the length of target traversed and arriving at the detector possess energies $E_1 > E_2 > E_3$. A theoretical proton spectrum of a material containing C in the bulk with a C-rich surface layer is given in Fig. 1. Thus shape of the peak may give information about the C content in the surface layer and in the bulk.

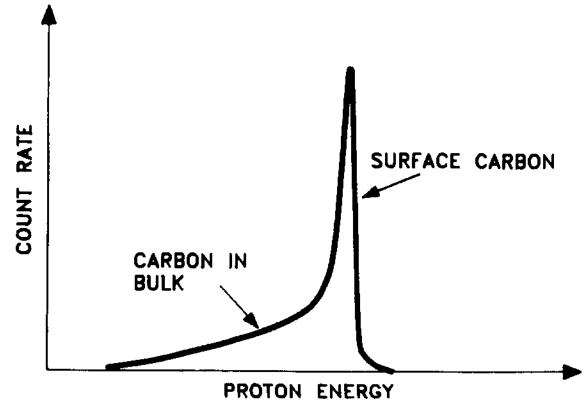

Fig. 1. A theoretical proton spectrum of material containing C with a C-rich surface layer.

The measurements were performed at 950 keV and 1420 keV deuteron energy in two different sample chambers. In the first one, the vacuum was about 5 × 10^{-6} mbar obtained using a turbomolecular pump; the detector was a PIPS silicon diode with active surface 300 mm^2 situated at 80 mm of the sample position and protected by a Al foil of 20 μm thick. The second one was a UHV chamber with a vacuum of about 10^{-9} mbar obtained using a cryogenic pumping system; in this case the detector is 64 mm from the sample position. In both cases the detection angle θ is 150°.

The beam current was between 20 and 80 nA depending on the different measurements and the diameter of the deuteron beam was a few mm^2. The counting time was about 10 min per data point. These conditions give a relatively low current density per unit area and minimize the effect of heating. Different preliminary tests have been performed concerning the adequate value of the current density: if the deuteron beam was too focused, the sample heated and became red at the impact point, generating a rapid decrease of the carbon content. In contrast, if the deuteron beam was large and the beam current weak, increasing carbon content was observed with the time when the measurements were made in the turbomolecular vacuum, due to contamination by the carbon contained in the residual vacuum of the target chamber.[9] Experimental conditions allowed these two phenomena to be limited.

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

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

where dA = number of detected particles = reaction peak area; Φ = number of incident particles = $Q/1{\cdot}6 \times 10^{-19}$, with Q = total incident charge measured by integrator (C); $d\sigma/d\Omega$ = differential cross section ($cm^2\ sr^{-1}\ nucleus^{-1}$); $d\Omega$ = 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 number.

The differential cross-section has been taken equal to 30 mbarns according to Ref. 10. The solid angle is $4{\cdot}69 \times 10^{-2}$ in the 5×10^{-6} mbar vacuum chamber and $7{\cdot}32 \times 10^{-2}$ in the UHV chamber.

Taking into account the ceramics density and the depth of the material analysed (0·4 μm), it is possible to deduce the carbon content in ppm (in weight) in the surface layer.

For 1420 keV energy incident deuterons, the carbon content has only been evaluated taking an average cross-section of 63·2 mbarns; At this energy, the material depth analysed is 4·4 μm; thus, if it is assumed that there is no gradient of concentration in function of the depth, the carbon content of the subsurface (between 0·4 and 4·4 μm) may be evaluated.

The authors have tried to clean the sample surfaces by different techniques:

(i) By polishing a ceramic surface with 3 or 6 μm diameter alumina or boron nitride powder dispersed or not in deionized distilled water, the C contents measured were increased by a factor close to 15, in comparison with those obtained before polishing, even after ultra-sound treatment.
(ii) The use of HF–HCl cleaning baths leads to the same results.
(iii) Finally, laser beam (λ = 532 nm of a YAG with a pulse width of 7 ns and a power of several hundreds of mJ cm^{-2}) cleaning gives the following results:
  —If the laser power is lower than the ablation threshold, the C content does not decrease.
  —The C content decreases only if the laser power is high enough to ablate the ceramic surface.

Taking into account the surface state of the materials and the statistical errors done in measurements, one can estimate that the carbon concentrations are accurate to 10%.

3 Results and Discussion

In the first part of the work, in the turbomolecular vacuum chamber, the carbon content was determined in ceramics which had the shape of cylinders 3 cm long and 8 mm diameter, sintered at 1300 and 1400°C.

Figure 2 shows a typical proton spectrum from (d,p) reaction in $BaTiO_3$ for 950 keV energy incident deuterons. It can be observed that the $^{12}C(d,p)^{13}C$ reaction peak is well separated on the spectrum. The surface layer of the as-sintered ceramics exhibits a carbon content of 5000 ppm whereas a fresh fracture made immediately before the introduction of the sample in the vacuum chamber exhibits a C content of 700 ppm. Results are very close for ceramics sintered at 1300 and 1400°C. At the incident energy used and under the experimental conditions (a large diode active surface in order to obtain good precision for the C contents), these peaks are essentially characteristic of the surface layer.

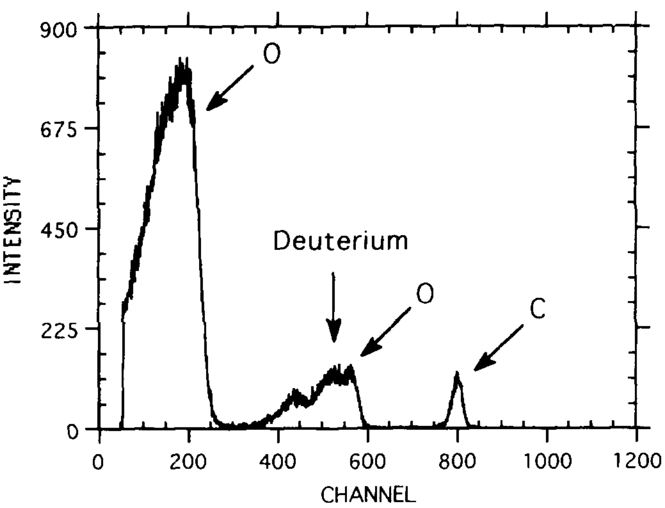

Fig. 2. The complete proton spectrum obtained from (d,p) reaction in $BaTiO_3$ ceramics with 950 keV deuterons.

For 1420 keV energy incident deuterons, the measurements permit the evaluation of the sub-surface C contents: 600 ppm for the 1400°C as-sintered ceramic and 50 ppm for the fresh fracture. For a ceramic sintered at 1300°C, the C content measured for the fresh fracture is more important.

If the fresh fracture is exposed in the air for two months, the measured C content remains constant. Thus, the surface is not contaminated by the atmospheric air and more particularly by atmospheric CO_2 which is generally adsorbed at the surface of all the materials.[3] This fact seems quite surprising because samples are ceramics with grain boundaries which may facilitate the adsorption of atmospheric gas. Freund *et al.*[11] indicated that a MgO single crystal freshly cleaved exhibited a low concentration but in a few days the C concentration rose, indicating a high carbon mobility in the MgO. These authors observed the same behaviour in olivine single crystals.[12] The carbon behaviour is thus different in the present case.

These results permit the formulation of the following remarks:

(i) The C content inside the ceramics is about 50 ppm.

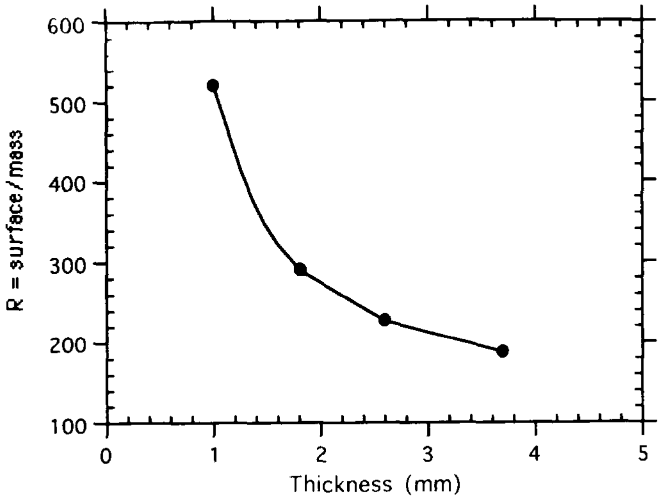

Fig. 3. Evolution of the C content in $BaTiO_3$ ceramic discs in function of the surface/mass ratio (see Table 1).

Table 1. Characteristics of the ceramics studied

	Disks				*Cylinder*
Thickness (mm)	1	1·8	2·6	3·7	
Surface area (mm^2)[a]	203	230	255	290	350
Mass (g)	0·39	0·79	1·12	1·54	2·24
C content (ppm)	350	410	440	2 000	3 500
R = surface area/mass (mm^2/g)	519	291	227	188	160

[a] Exchange surface with atmosphere.

(ii) When the ceramic is fractured, carbon is surely adsorbed on the fresh surface in the seconds which follow the fracture. Then an equilibrium is established between the carbon of the atmosphere and the carbon in the surface layer of the samples.

(iii) In these conditions, it is possible to roughly evaluate the carbon content due to the contamination and that which is intrinsic to the as-sintered ceramics. The effect of the contamination is not the principal origin of carbon.

(iv) The residual carbon content detected in the surface layer seems to originate essentially in diffusion from the bulk during the sintering step. The higher the sintering temperature, the lower the carbon content in the bulk.

In the second part of the work, the influence of the shape of the ceramics on the residual carbon content in the surface layer has been studied. Discs of 1 cm diameter and variable thicknesses have been sintered at 1400°C and the surface layer C content measured with 950 keV deuterons in the UHV chamber. The results obtained are presented in Table 1 and in Fig. 3.

A cylindrical ceramic has also been studied and the results are reported in Table 1.

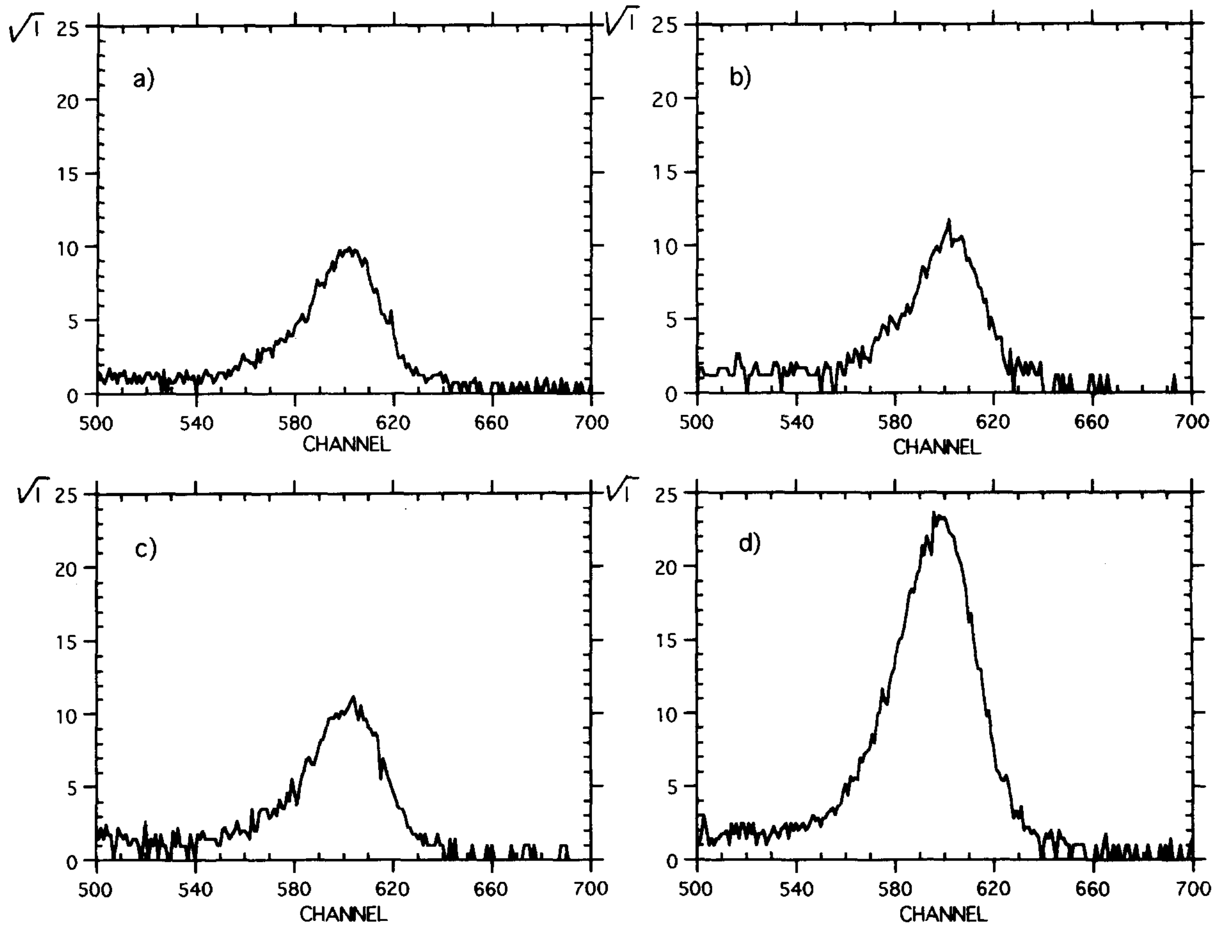

Fig. 4. The C peaks of the proton spectra obtained from 950 keV deuterons for ceramic discs of different thickness: (a) 1 mm; (b) 1·8 mm; (c) 2·7 mm; (d) 3·6 mm.

An increase in the C content is observed when the sample thickness increases and the exchange surface decreases (Fig. 4). The C peak shapes show a relatively more important contribution of the subsurface layer for a less thick sample.

These results confirm the diffusion of C from the bulk during the sintering step. When the ceramic is thin, carbon may easily and quickly diffuse from the bulk to the surface then to the atmosphere. When the thickness increases, the carbon quantity in the sample increases and as the exchange surface decreases, the diffusion is slower.

It is also interesting to note that a cylindrical sample exhibits a surface C content of 3500 ppm in a 10^{-9} mbar vacuum and 5000 ppm in a 10^{-6} vacuum. It can be considered that (i) under 10^{-9} mbar the carbon weakly bound to the ceramic is desorbed or (ii) under 10^{-6} mbar, the carbon contained in the residual vacuum may contaminate the surface of the ceramic. As no increase in the C content was measured after an exposure of a freshly fractured sample to air for two months, the first hypothesis seems to be the most probable. This points out the influence of the vacuum on the detected C contents.

4 Conclusion

The results obtained in this first study are summarized as follows:

(i) $BaTiO_3$ ceramics synthesized by the citric resin route exhibit residual carbon contents. The C concentration is not uniformly distributed: it is higher at the surface and decreases toward the bulk.

(ii) In the surface layer (0·4 μm) two types of carbon exist:
 —Carbon only adsorbed on the surface which is easily desorbed under UHV conditions. It could originate from atmospheric contamination.
 —Material intrinsic carbon. It is not desorbed in the UHV conditions or by laser beam cleaning.

(iii) In the subsurface (0·4 to 4·4 μm) the C content has been evaluated assuming a constant concentration as a function of the depth; in fact there exists a gradient of concentration from the surface to the heart for which the C content has been evaluated to be very low (about 50 ppm).

(iv) The C contents depend on the sintering conditions of the ceramics: carbon existing in $BaTiO_3$ powders after calcination of the citric resins at 700°C, diffuses during the sintering step from the bulk to the surface. This explains the difference of C content observed in the surface layer and in the bulk more especially as the exchange surface with the atmosphere is weaker.

(v) The C content determined on a freshly fractured surface does not increase with the time even after an exposure in the air for two months. Thus, the carbon contained in the bulk does not exhibit a high mobility. The study of the chemical form of the carbon in the ceramics is actually in progress.

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