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XPS Investigation of Surface Properties of $Ba_{(1\text{-}x)}Sr_xTiO_3$ Powders Prepared by Low Temperature Aqueous Synthesis

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Abstract

Barium titanate powders prepared by wet chemical routes are known to show large deviation from stoichiometry and contamination at surface, due to chemical instability in solution at low pH values ($<$ 9), and carbonates formation after exposition to air. The surface composition of ceramic powders prepared via the low temperature Aqueous Synthesis (LTAS), with nominal formula $Ba_{(1-x)}Sr_xTiO_3$ *(*$x \leq 0{\cdot}1$*), have been investigated on pressed pellets of as-prepared powders by X-ray photoelectron spectroscopy.* $BaCO_3$ *content has been evaluated from Ba3d and Ba4d spectra. The total relative amount of carbonate has been measured by X-ray diffraction and compared to that present on surface. From these data, the formation of* $BaCO_3$ *by surface reaction with the atmosphere or by bulk precipitation is discussed. © 1999 Elsevier Science Limited. All rights reserved*

Keywords: powders, electron spectroscopy, $BaTiO_3$.

1 Introduction

During last decades a wide number of chemical syntheses have been proposed for the preparation of ceramic powders, especially for Barium Titanate ($BaTiO_3$) and related compounds.[1–3] Most of these routes are well designed to prepare small sized, pure and stoichiometric particles, either dispersed or arranged into films. Major drawbacks of such techniques are represented by the chemical contamination from foreign atoms entering the processes and the formation of secondary phases, like carbonates, due to the employment of alkaline solutions[4] or thermal decomposition of organic precursors.[5] Moreover, the washing procedures that are commonly adopted to eliminate impurities can significantly alter stoichiometry through preferential leaching of Barium from the surface.[6] The Low Temperature Aqueous Synthesis (LTAS) is a route suited for the preparation of Barium and Strontium Titanates, Stannates, Zirconates and Hafniates,[7] that has been also applied to the synthesis of donor-doped $(Ba,Sr)TiO_3$ solid solutions for the realisation of PTCR ceramics.[8] Recently[9] it has been pointed out that the size of $BaTiO_3$ particles can be tailored, around 25–50 nm, by simply changing the value of some physical parameters of the LTAS process: on the contrary, the carbonation degree is virtually unaffected, being mostly determined by exposure to air of alkaline solutions.

Surface purity of powders prepared by such a method has never been directly investigated until now and little has been published about $BaTiO_3$ obtained by other techniques. X-ray photoelectron spectroscopy (XPS) has been used by Hung *et al.*[10] and Herard *et al.*[11] to detect the presence of a thin layer of $BaCO_3$ on $BaTiO_3$ particles surface prepared by the hydrothermal and by the oxalates routes, while Miot *et al.*[12] investigated by the same technique the residual carbon content both on $BaTiO_3$ powders and ceramics prepared via the citric route, obtaining similar results.

In order to investigate the barium carbonate distribution and to detect the presence of foreign atoms which could affect the electrical properties of sintered ceramics, powders with nominal composition $Ba_{(1-x)}Sr_xTiO_3$ ($x = 0$, $x = 0{\cdot}1$) prepared by the LTAS method have been characterised by XPS, a technique that allows the analysis of the outermost layers (2–4 nm) of particles. The effective surface

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covering of particles with Si, a well known sintering aid added during the ageing phase, has been checked also.

2 Experimental

Powders were obtained through the reaction

$$(1-x)\mathrm{Ba(OH)_2} + x\mathrm{Sr(OH)_2} + \mathrm{TiCl_4} + 4\mathrm{NaOH}$$
$$\mathrm{Ba_{(1-x)}Sr_xTiO_3} + 4\mathrm{NaCl} + 3\mathrm{H_2O}$$

carried out in a PTFE batch reactor at 80°C, under flowing desiccated N_2 at atmospheric pressure.[13] After precipitation, the particles were aged in the same solution at 80°C for 5 h, washed with distilled water and eventually dried in air at 100°C. The addition of Si (1000 ppm) as colloidal silica (Aldrich Chemicals) was realised in BST2 sample at the beginning of ageing, while in BST3 sample it was added by conventional wet ball milling, after washing and drying. BST4 sample was prepared by solid state route: stoichiometric amounts of $BaCO_3$, $SrCO_3$ and TiO_2-rutile (Fluka Chemica) were mixed by wet ball milling, dried, sieved and calcined in air at 1100°C for 2 h. Table 1 reports samples nominal composition and average particle size, estimated by scanning electron microscope (SEM) observations.

Specimens for the XPS analyses were prepared by compacting sieved powders at 150 MPa under isostatic pressure into pellets. They were broken just before insertion into the high-vacuum chamber of the spectrometer (Physical Electronics Inc., ESCA 5600 Multitechnique) in order to minimise handling contamination: in some cases a previous thermal treatment at 300°C was necessary to reduce water outgassing from the compacts. The X-ray radiation was generated by a monochromated Al source (1 mm spot size) and the spherical electron energy analyser operated in the fixed analyser transmission (FAT) mode at a constant pass energy of 29·35 eV.

Because of the charging of insulating samples, an electron flood gun was applied to neutralize the net positive surface charge; the emission current used was 17 mA. Photoelectron spectra of Ba3d, Ba4d, O1s, C1s and Ti2p bands were recorded, setting the C–C binding energy at 284·6 eV. Fitting of collected spectra was carried out by the software Multipack V2·2A (Physical Electronics Inc.), using mixed Gaussian-Lorentzian functions. Specimens from the same batches were characterised by X-ray diffraction (XRD), using a powder diffractometer (Philips, PW1710, Co $K\alpha$ radiation) in the Bragg–Brentano configuration. The relative carbonate content was determined by the Rietveld method and all calculations were performed within the Cerius^2 environment (Molecular Simulations Inc., San Diego, CA). The structures of cubic $Ba_{(1-x)}Sr_xTiO_3$ and of orthorhombic $BaCO_3$ were assumed as reference models; data were taken from the inorganic crystal structure database[14] (cards number 27970 and 15196). Fitting procedure took into account as many as 20 parameters, comprising lattice constants, angle dependent asymmetries and aberrations, peak profile shape functions and background subtraction.

Table 1. Norminal composition, synthesis method, and average particle size of $Ba_{(1-x)}Sr_xTiO_3$ powders prepared

Sample	x *(nominal)*	*Synthesis*	*Additives*	*particle size d (nm)*
BT	0	LTAS	—	30
BST1	0·1	LTAS	—	30
BST2	0·1	LTAS	Si (1000 ppm)	30
BST3	0·1	LTAS	Si (1000 ppm)	30
BST4	0·1	solid state	—	500
BST5	0·1	LTAS	—	30

3 Results

As-prepared powders showed at XRD analysis crystalline structure with cubic or pseudocubic symmetry, with hardly detectable contribution from a secondary Ti-rich phase in BST1 sample. As reported in Table 2, the relative barium carbonate content, $BaCO_3/Ba_{(1-x)}Sr_xTiO_3$ (BC/BST), was highly variable from batch to batch, ranging

Table 2. XRD and XPS results

Sample	*BC/BST XRD Molar ratio (%)*	*BC/BST XPS (Ba 3d) Molar ratio (%)*	*BC/BST XPS (Ba 4d) Molar ratio (%)*	$(Sr/Ba)_{tot}$ *XPS (Ba 3d) Molar ratio (%)*	$((Ba+Sr)/Ti)_{BST}$ *XPS (Ba 4d) Molar ratio (%)*	*Impurities (at%)*
BT	6·16	32	15	11	74	—
BST1	11·1	229	180	18	29	—
BST2	3·31	64	60·3	21	106	Si (2), Cl (5)
BST3	1·63	39	30·3	32	99	Si (4), N (1)
BST4	0·50	58	25·8	23	92	K (0·5)
BST5	2·04	54	40·5	22	69	—

$BC = BaCO_3, BST = Ba_{(1-x)}Sr_xTiO_3$.

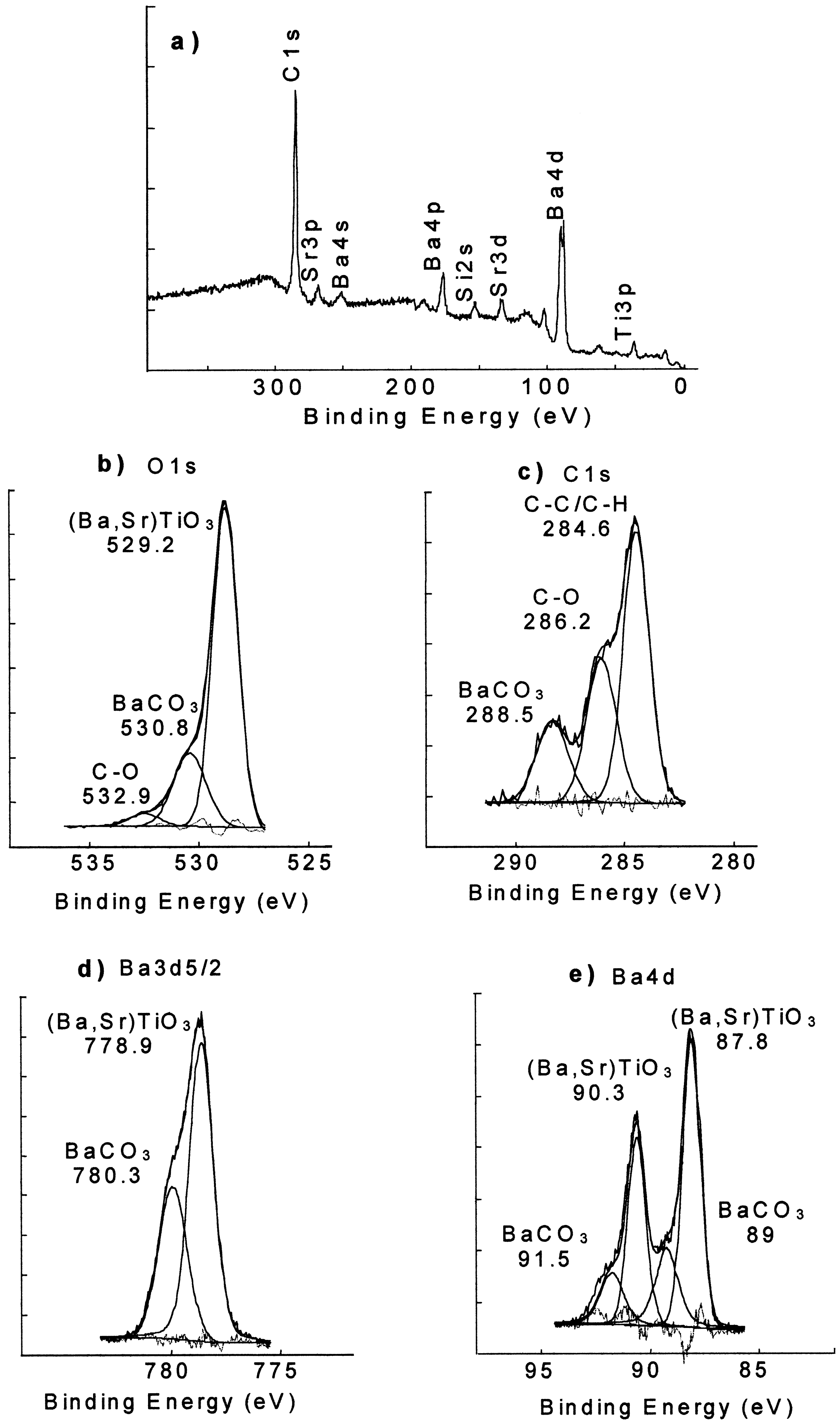

Fig. 1. XPS spectra relative to (a) BST2 and (b)–(e) BST5 samples.

between 1·6 and 11 at%. Only the sample prepared by solid state reaction (BST4) showed a low carbonation level (0·5 at%), due to the calcination at 1100°C. XPS surveys revealed, beside Ba, Sr, Ti, O and C, the presence of Si [Fig. 1(a)] with a molar ratio of 2–4 at%, one order of magnitude higher than the nominal amount (see tables), only in the samples intentionally added with this element (BST2, BST3). Other impurities can be supposed to originate from occasional ineffectiveness of washing (Cl), reagents impurities (K) and post-washing treatments (N). General features of XPS spectra shown in Fig. 1(b)–(e), relative to BST5 sample, are representative of all samples analysed and consistent with literature data. In particular, the C1s band can be resolved into the C–C/C–H line at 284·6 eV, the $BaCO_3$ line at 288·5 eV and a line at 286·2 eV, reported[12] as a C–O group. This line appears also in the O1s band at 532·9 eV, together with the $(Ba,Sr)TiO_3$ and the $BaCO_3$ lines at 529·2 and 530·8 eV, respectively. The presence of $BaCO_3$ is evident from the 3d and 4d transition bands of barium as well: Ba3d5/2 peak is composed by the titanate line at 778·9 eV and the carbonate one at 780·3 eV[11,12], similarly to the Ba4d band that can be resolved in two doublets, at 87·8–90·3 (titanate) and 89–91·5 eV (carbonate).[10] Finally, the Ti2p band appears in each sample as a unique doublet at 457·9–463·6 eV, indicating that no Titanium compound other than $(Ba,Sr)TiO_3$ was formed. The relative amount of different elements in the various chemical species was evaluated from peaks areas and calculated values are reported in Table 2.

Surface stoichiometry can be reported as the total Sr/Ba molar ratio or as the (Ba + Sr)/Ti molar ratio in the titanate phase: both parameters reveal large deviations from nominal values, caused by the incorporation of Ba atoms into the carbonate phase and influenced by the simultaneous presence of impurities.

4 Discussion

It is known that detectable Ba3d photoelectrons originate at no more than 2 nm under the particles surface, while Ba4d band gives information about a deeper layer (approx. 5 nm[10]) because of the much lower binding energy of electrons in this state. As a consequence, the reduction of the BC/BST ratio passing from Ba3d to Ba4d band, common to all BST samples, proves that a layer of $BaCO_3$ is present on the particles surface. The thickness of this layer, formed by reaction of Ba with CO_2 after the synthesis, can be estimated between 1 and 3 nm. From Table 2 it can be noted that the total carbonation of powders cannot be inferred from XPS measurements only; in fact, taking also into account XRD data, even powders with remarkably different $BaCO_3$ content can result very similar at XPS analyses, like for BST4 and BST5 or BT and BST3 samples.

Such apparent similitude in the first case is due to the difference in particle sizes (500–30 nm) that makes the surface/volume ratio of these powders significantly different and, assuming a constant thickness for the carbonate layer, mainly affects the volume concentration given by XRD. The second case cannot be explained with size effects but only on the grounds of the formation of a carbonate phase mostly distributed either as separate particles or into the bulk of $BaTiO_3$. However, as no evidence of separate acicular $BaCO_3$ particles was found in SEM images of BT sample, a simultaneous formation of titanate and carbonate in the LTAS process appears more probable in this case. From reported XPS data, a clear indication about the distribution of SiO_2 can be drawn: it is possible to cover the surface of titanate particles with Si by addition of this element during LTAS ageing. This can be regarded as an advantage of such technique as the introduction of a sintering aid on the particles surface is already realised during the synthesis, without further treatments.

5 Conclusions

XPS analyses, performed on $Ba_{(1-x)}Sr_xTiO_3$ powders prepared by LTAS route, indicated the presence of a $BaCO_3$ layer at the surface, originated by contamination after the synthesis stage. The combination of XRD and XPS data pointed out the possibility of a different carbonation mechanism in the LTAS process, probably during the precipitation-ageing stage, leading to the formation of $BaCO_3$ in the bulk of titanate particles.

XPS measurements also demonstrated that silica introduced during LTAS ageing was preferentially distributed at the surface of titanate particles, showing the possibility of direct addition of sintering aids avoiding any milling treatment.

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