Characterization of BaTi$_4$O$_9$ ceramics by Raman spectroscopy and XPS after ion etching

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Barium tetratitanate (BaTi$_4$O$_9$) ceramic prepared by coprecipitation method was analyzed by Raman spectroscopy and by X-ray photoelectron spectroscopy (XPS). The orthorhombic crystalline structure of BaTi$_4$O$_9$ ceramic sintered at 1300 ºC for 2h in air was identified on the Raman spectrum. The sample was etched in argon plasma and then analysed by XPS. The etching process did not influence significantly the XPS spectra of barium and titan suggesting a good compositional homogeneity of the BaTi$_4$O$_9$ ceramic prepared by oxalate method.

1. Introduction

Titania rich compounds in the BaO-TiO$_2$ system (such as BaTi$_4$O$_9$ and Ba$_2$Ti$_9$O$_{20}$) are used to obtain miniaturised microwave resonators, with high dielectric constants [1-4]. The electronic behaviour of the barium titanates is correlated both with bulk and interfacial characteristics. Consequently, many features, especially the bulk properties such as the crystal structure, evolution of grain growth and imperfections have been studied. The electrical properties of BaTi$_4$O$_9$ also depend on the chemical states of the constituents and on the surface chemistry of the specimens. The presence of any contaminants on the surface or an alteration in its composition can affect the electrical characteristics of BaTi$_4$O$_9$. However, information on the chemical states of the ions and surface chemistry of the material in relation to its properties is very limited.

In this paper, Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) studies on sintered BaTi$_4$O$_9$ discs are presented. Raman spectroscopy gives information about the crystalline phases present in the bulk. Javadpour and Eror [5] used Raman spectroscopy as an integral method to analyse wet-chemically prepared Ba-Ti precursors of the phases BaTi$_2$O$_5$, Ba$_6$Ti$_{17}$O$_{40}$, Ba$_4$Ti$_{13}$O$_{30}$, BaTi$_4$O$_9$, Ba$_2$Ti$_9$O$_{20}$, and BaTi$_5$O$_{11}$, and their thermal stability. XPS is a surface analytical technique providing information on the chemical states of the constituents. A correlation between crystalline structure and composition of BaTi$_4$O$_9$ ceramics is presented in this paper.

2. Experimental procedure

2.1. Sample preparation

BaTi$_4$O$_9$ powders were prepared by an oxalate coprecipitation method described in a previous paper [6]. Aqueous solution of barium chloride (BaCl$_2$·2H$_2$O),

titanium tetrachloride (TiCl$_4$), and ammonium oxalate ((NH$_4$)$_2$C$_2$O$_4$·H$_2$O) were chosen as starting materials for synthesis of BaTi$_4$O$_9$. The mixed solution of barium chloride and titanium tetrachloride was added to the aqueous solution of ammonium oxalate to obtain the precipitate. After filtration, the precipitate was washed in ammoniacal water (pH 8) to avoid the loss of Ba^{2+} and Ti^{4+}. The washing is done for complete elimination of Cl$^-$ and C$_2$O$_4$$^{2-}$ ions. Then, the precipitate was dried at 100°C and calcined at high temperature (≤1300°C) to form the single-phase compound. BaTi$_4$O$_9$ with orthorhombic symmetry was obtained by sintering at 1300 ºC for 2 h of as-prepared precipitate precursor [6]. The calcined BaTi$_4$O$_9$ powder was pressed into disks at a pressure of 200 MPa and sintered at 1300 °C for 2h in air. These pellets were characterized by Raman spectroscopy and XPS.

2.2. Raman and XPS measurements

The Raman spectrum was recorded at room temperature using a R-2001^{TM} Spectrometer. The 785 nm line of a laser operating at 500 mW was used for excitation. XPS spectra were recorded with a VG Esca II Mk3 spectrometer using monochromatized Al-Kα radiation (1486.6 eV). The analysis chamber was maintained at ultra high vacuum (~2·10^{-9} torr) and the sample position was oriented at an angle θ = 45 º in respect to the analyzer. The XPS spectra were recorded with an energy window of 20 eV and a resolution of 50 eV. Data collection was accomplished using a computer-interfaced digital pulse counting system. The XPS spectra were processed using Spectral Data Processor v2.3 (SDP) software which allow smoothing and deconvolution of the curve. The sample was exposed 15 min to plasma etching in a preparation chamber at the argon pressure of about 5×10^{-6} torr, 5 kV accelerating voltage for argon ions and 4

kV focus voltage. As the standard practice in XPS studies, the carbon line (C 1s, 285 eV) corresponding to the C-C bond has been used as standard.

3. Results and discussion

3.1. $BaTi_4O_9$ crystalline structure

The crystal structure of the $BaTi_4O_9$ compound was reported by several groups [7-9], and it was shown to be isostructural with orthorhombic KTi_3NbO_9 [10]. Barium tetratitanate crystallises in the orthorhombic system, with Pmmnz space group and the unit cell parameters: 14.527(2), 3.794(1) and 6.293(1) Å [7] (Fig.1). The $BaTi_4O_9$ compound is caracterized by the presence of the pentagonal prisme tunel structure [11]. The tunel structure brings about a significantly large distortion of TiO_6 octaedra.
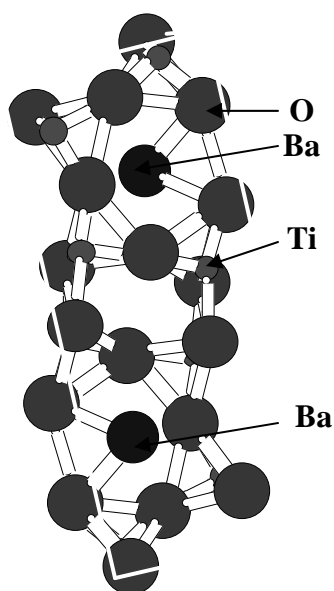

Fig. 1. Orthorhombic structure of barium tetratitanate-$BaTi_4O_9$.

The crystalline structure of $BaTi_4O_9$ compound shows Ba-O, Ti-O and O-O bonds (Fig.1).

3.2. Raman spectra

We recorded the Raman spectrum of $BaTi_4O_9$ samples at room temperature. This spectrum shows peaks at 236, 333, 431, 639 cm^{-1} and at 847 cm^{-1} (Fig. 2). Comparing our results with data from the literature [12], these peaks indicate the orthorhombic crystalline structure of $BaTi_4O_9$.
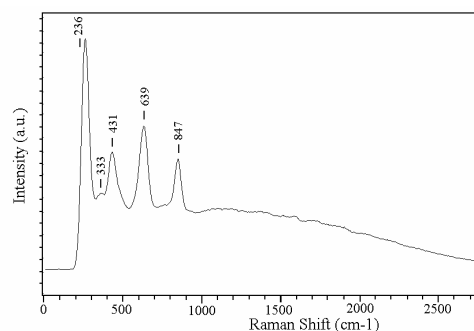

Fig.2. Raman spectrum of $BaTi_4O_9$ ceramic.

No other peaks were detected in the Raman spectrum, suggesting that the sample consists from a single-phase compound ($BaTi_4O_9$), in good agreement with XRD data presented in previous paper [6].

3.3. XPS spectra

To determine the chemical species on the $BaTi_4O_9$ sample surface, XPS spectra were recorded in the range of C 1s, O 1s, Ba 3d, and Ti 2p core-level photo-emission lines. The deconvoluted spectra of C 1s, O 1s, Ba 3d and Ti 2p lines obtained from a $BaTi_4O_9$ sample before plasma etching are shown in Figs.3 – 6 respectively.
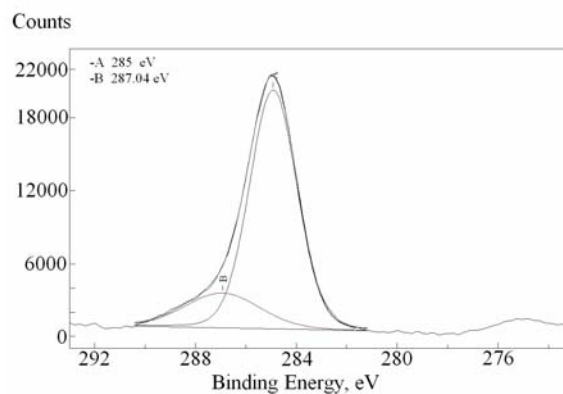

Fig. 3. Spectra of C 1s line for $BaTi_4O_9$ ceramic before etching.

Carbon C 1s line can be deconvoluted into two lines with peaks at 285 eV - corresponding to carbon bonded with another carbon (C-C) and at 287.04 eV - due to carbon bonded with oxygen (C-O). The amount of the carbon atoms bonded as C-C and as C-O is 81.3 %, respectively 18.7 %. These values suggest that the carbon identified by XPS spectroscopy in all the samples due to the environmental contamination, is present as adsorbed carbon and adsorbed CO_2. The peaks corresponding to barium carbid, titanium carbid or barium carbonate are absent in the XPS C 1s spectrum of $BaTi_4O_9$ ceramic before etching (Fig.3).

The O 1s photoelectron curve (Fig.4.a) of not etched $BaTi_4O_9$ sample has two components resulted from curve

fitting. The O 1s emission line at 532.04 eV is attributed to the adsorbed oxygen as O-C of CO_2 [13], and the O 1s line at 530.07 eV corresponds to the oxygen bonded in $BaTi_4O_9$ as oxygen-metal bonds.
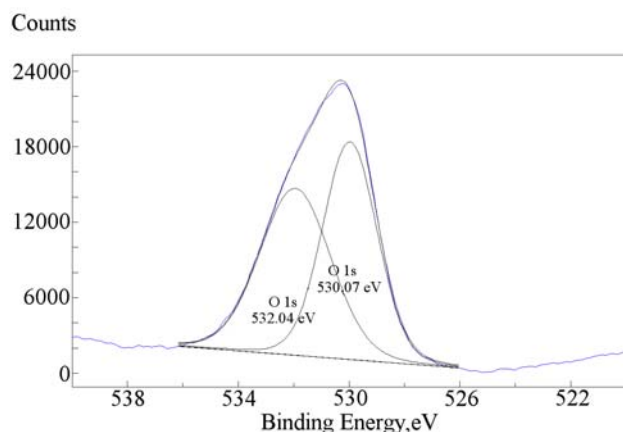

Fig. 4. Spectra of O 1s lines of BaTi₄O₉ ceramic before etching.

Quantitatively, 50 % of the oxygen is bonded as O-metal and the remaining 50 % oxygen is bonded as O-C.

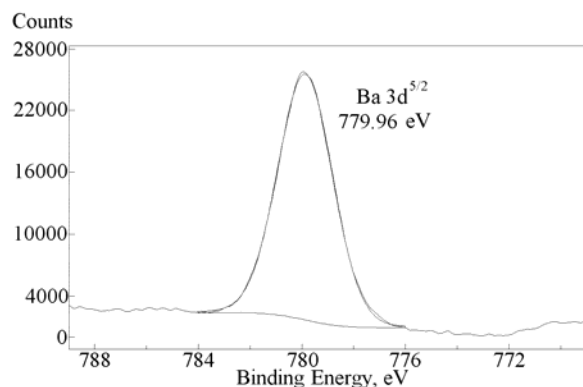The Ba $3d^{5/2}$ photoelectron signal exhibits only a peak at 779.96 eV (Fig. 5).

Fig. 5. Spectrum of Ba 3d line of BaTi₄O₉ ceramic before etching.

The curve is attributed to Ba bonded to oxygen in the lattice of $BaTi_4O_9$.

The Ti 2p spectrum, shown in Fig.6, has two components, Ti $2p^{1/2}$ and Ti $2p^{3/2}$. The fitted Ti 2p spectrum shows the main peaks assignated to Ti $2p^{1/2}$ and Ti $2p^{3/2}$ centred at 464.13 eV and 458.46 eV respectively, which are in good agreement with the literature regarding the bonding energies of Ti^{4+} in barium titanate [14].
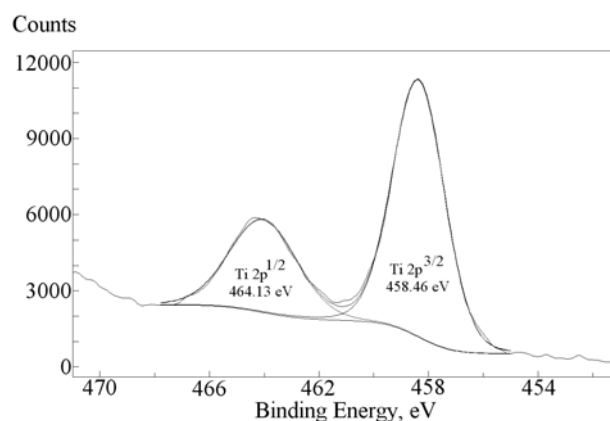

Fig. 6. Spectra of Ti 2p lines of BaTi₄O₉ ceramic before etching.

The peaks assignared to Ti $2p^{1/2}$ and Ti $2p^{3/2}$ correspond to the main peak and are separated by ~1.5 eV. The principal components (Ti $2p^{1/2}$) and Ti $2p^{3/2}$ are attributed to Ti in Ti^{4+} normal state in the $BaTi_4O_9$ lattice. The litterature indicates bonding energies for Ti^{4+} in the range from 458.5 eV to 459.2 eV in TiO_2 [15, 16] and 456.9 eV - 457.8 eV for Ti^{3+} in Ti_2O_3 [17]. The Ti 2p spectrum shown in Fig.6, suggests that the Ti^{3+} ions are not present in our $BaTi_4O_9$ sample.

The samples were etched to remove surface contamination (with oxygen and carbon). This process achieved a semnificative reduction in the intensities of C (1s) lines and the higher energy components of the O (1s) spectra indicating the generation of cleaner surfaces (Figs.7-10).

As shows the Fig. 7, the carbon C 1s XPS spectrum consists of two peaks; one peak centred at 285 eV, corresponding to C-C bonds (89 % from the atoms of carbon participate to this kind of bond) and the other one at 287.02 eV attributed to the 11 % of the carbon atoms bonded as C-O.
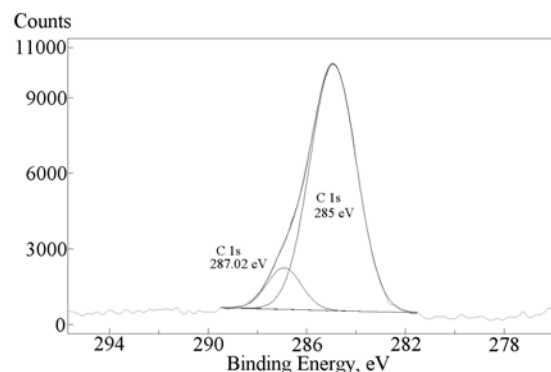

Fig. 7. Spectra of C 1s line for BaTi₄O₉ ceramic after etching

This result indicates a change of the carbon bonded as C-C / carbon bonded as C-O ratio by etching wits from 18.7 % to 11 %, and the carbon contamination of $BaTi_4O_9$ samples decreases from 57.60.% to 30.31.% in atomic percent (Tab. I).

The O 1s spectrum of etched $BaTi_4O_9$ sample (Fig.8) shows two peaks at 530.15 eV of the oxygen bonded as O-metal and, at 531.14 eV corresponding to oxygen contamination (O-C bond).
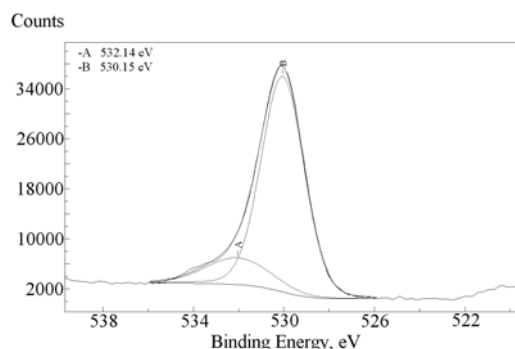

Fig. 8. Spectra of O 1s lines of $BaTi_4O_9$ ceramic after etching

The atomic (%) ratio O_{O-M}/O_{O-C} =84.1/15.9 indicates that the adsorbed oxygen does not disappear by etching in the above mentioned conditions.

The spectrum of Ba $3d^{5/2}$ line of $BaTi_4O_9$ ceramic after etching (Fig.9) shows a single peak at 780.15 eV corresponding to its bonds with oxygen atoms.
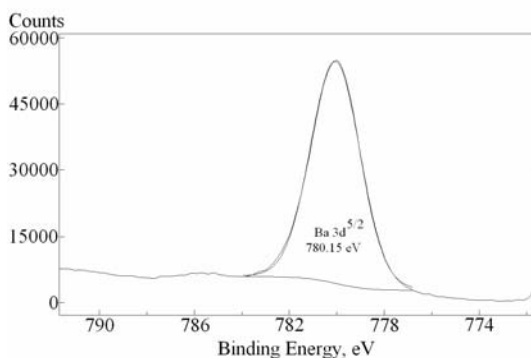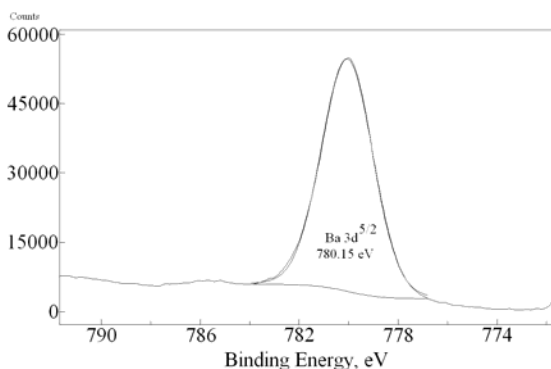

Fig. 9. Spectrum of Ba 3d line of $BaTi_4O_9$ ceramic after etching

The intensity of Ba 3d line increases after etching the surface of the $BaTi_4O_9$ sample.

The Ti 2p photoelectron curve (Fig.10) of the etched $BaTi_4O_9$ ceramic has four components resulted from the curve fitting. The peaks Ti $2p^{1/2}$ of 463.74 eV (A) and Ti $2p^{3/2}$ of 458.09 eV (B) correspond to Ti from TiO_2.
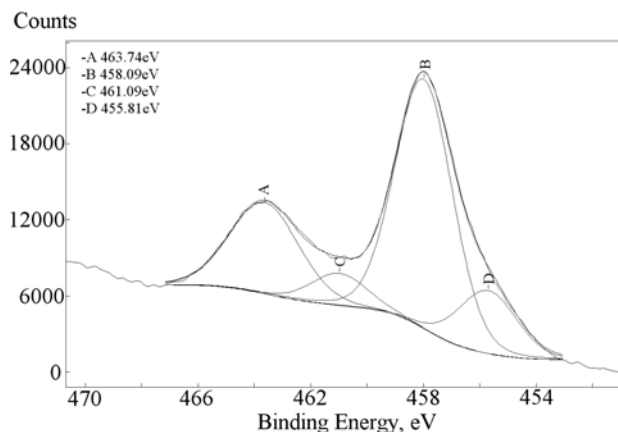

Fig. 10. Spectra of Ti 2p lines of $BaTi_4O_9$ ceramic after etching

The peaks Ti $2p^{1/2}$ of 460.89 eV (C) and Ti $2p^{3/2}$ of 456.01 eV (D) correspond to Ti from TiO. Only, 25 % from the titanium atoms form TiO groups.

The intensity and the shape of Ba 3d and Ti 2p lines are not significantly changed after etching the $BaTi_4O_9$ sample surface, suggesting a homogeneous repartition of Ba and Ti at the surface and in the bulk of the sample. The chemical compositions of $BaTi_4O_9$ sample surface, before and after etching, determined by using Spectral Data Processor v2.3 (SDP) software, are presented in Tabble I.

Table 1. Chemical composition of the surface of $BaTi_4O_9$ ceramic (at.%):

	C	O	Ti	Ba
Before etching	57.60	33.79	5.21	3.4
	-	-	60.49	39.51
After etching	30.31	45.30	15.91	8.48
	-	-	65.21	34.79

The composition ratio of Ba and Ti changes indicated a small enrichment of Ti on the etched surface caused by the sublimation of Ba during ionic beam sputtering with Ar^+ of the $BaTi_4O_9$ surface, or by segregation of Ti from the bulk.

4. Conclusions

The Raman spectrum of ceramic sample obtained by sintering at 1300 ^{o}C for 2 h, the precipitate precursor indicates an orthorhombic crystalline structure for $BaTi_4O_9$.

XPS spectra recorded in the range of the C 1s, O 1s, Ba 3d and Ti 2p core-level photoemission lines before and after argon ion cleaning indicate the presence of Ba^{2+}, Ti^{4+}, O^{2-} and C in the $BaTi_4O_9$ ceramic pellets.

The etching process with Ar^+ ions of the $BaTi_4O_9$ sample caused a semnificative reduction in the intensities of C (1s) lines and of the O (1s) spectra, indicating the cleaning of the sample surface. No major spectral changes were produced for the Ba 3d and Ti 2p recorded spectra following the etching.

Raman spectroscopy and XPS studies indicate that the ceramic prepared by coprecipitation with oxalic acid consists from a homogeneous single-phase compound (BaTi$_4$O$_9$) with orthorhombic crystalline structure.

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