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RESEARCH ARTICLE

XPS CHARACTERIZATIONS OF PB $(ZR_X,TI_{1-X})O_3$ CERAMICS

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ABSTRACT

Lead titano-zirconate (PZTx), with different concentrations in Zr (x ranging from 26 to 78), was synthesized by the conventional solid state reaction route. Pellets annealed at 900°C during 4 hours have been characterized by X-Ray Photoelectron Spectroscopy (XPS). Determination of the constituents at the surface of the samples from XPS analysis has given good agreement with nominal compositions.

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INTRODUCTION

Pb (Zr_x,Ti_{1-x}) O_3, (PZTx) is a perovskite-type ceramic which exhibits piezo-electric, pyroelectric and ferooelectric effects which are of great importance for industrial applications such as ultrasonic transducers and ceramic capacitors. PZT material has been elaborated for the first time, in 1952, by Yutaka Takagi *et al.* from Institute of technology's of Tokyo (T. Lamcharfi *et al.*, 2005). XPS characterization permits a chemical analysis at interfaces between deposited layers and their substrate, and identification of surface contaminations of materials (Davoisne, 2006; Ohring, 1992; Ababou, 1996). In XPS experiment the sample is illuminated with soft X-radiation in an ultrahigh vacuum; the photoelectric effect caused by the X-rays leads to the generation of photoelectrons, the energy spectrum of which can be determined in a beta-ray spectrometer. The energy spectrum permits determination of the composition of the sample. We have used this technique to study PZTx samples, x = 0.26, 0.39, 0.52, 0.65 and 0.78, and have compared the nominal compositions to those extracted from XPS analysis.

Experimental details

PZTx powders were prepared using the conventional solid state reaction technique. The latter consists of a simple mixing of PbO, TiO_2, and ZrO_2 oxides. XPS measurements were performed on pellets heat treated at 900°C during 4h. The XPS used was a Kratos Axis-Ultra equipped with a magnetic-electrostatic hybrid lens. The analyzed region was about 400 microns x 800 microns, with a monochromatic Al Kα source at 300 W. The X-ray angle of deviation in respect to the normal to the samples was 60°. XPS experiments were conducted in an ultra-high vacuum environment (8×10^{-10} Torr).

RESULTS AND DISCUSSION

Fig.1 illustrates XPS survey spectra of PZTx samples. Analysis of these spectra revealed the presence of Al, C, Ca, Cl, O, Pb, Si, Ti, Zn and Zr. Table 1 gathers concentrations of the elements detected at the surface of the samples. These are pollutants which may come from basic chemical products or from used equipments. This is also the case of carbon which has a relatively high concentration and which is probably present in the form of hydrocarbons adsorbed at the surface. Table 2 gives nominal compositions of the PZT samples and those estimated from XPS analysis a good agreement is

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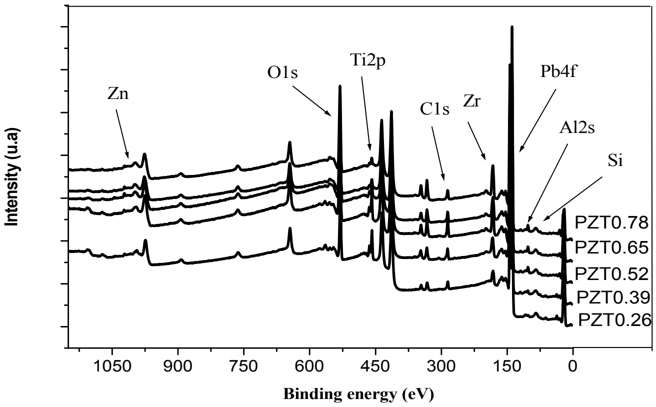


Figure 1. XPS spectra of PZTx samples heat treated at 900°C during 4 hours

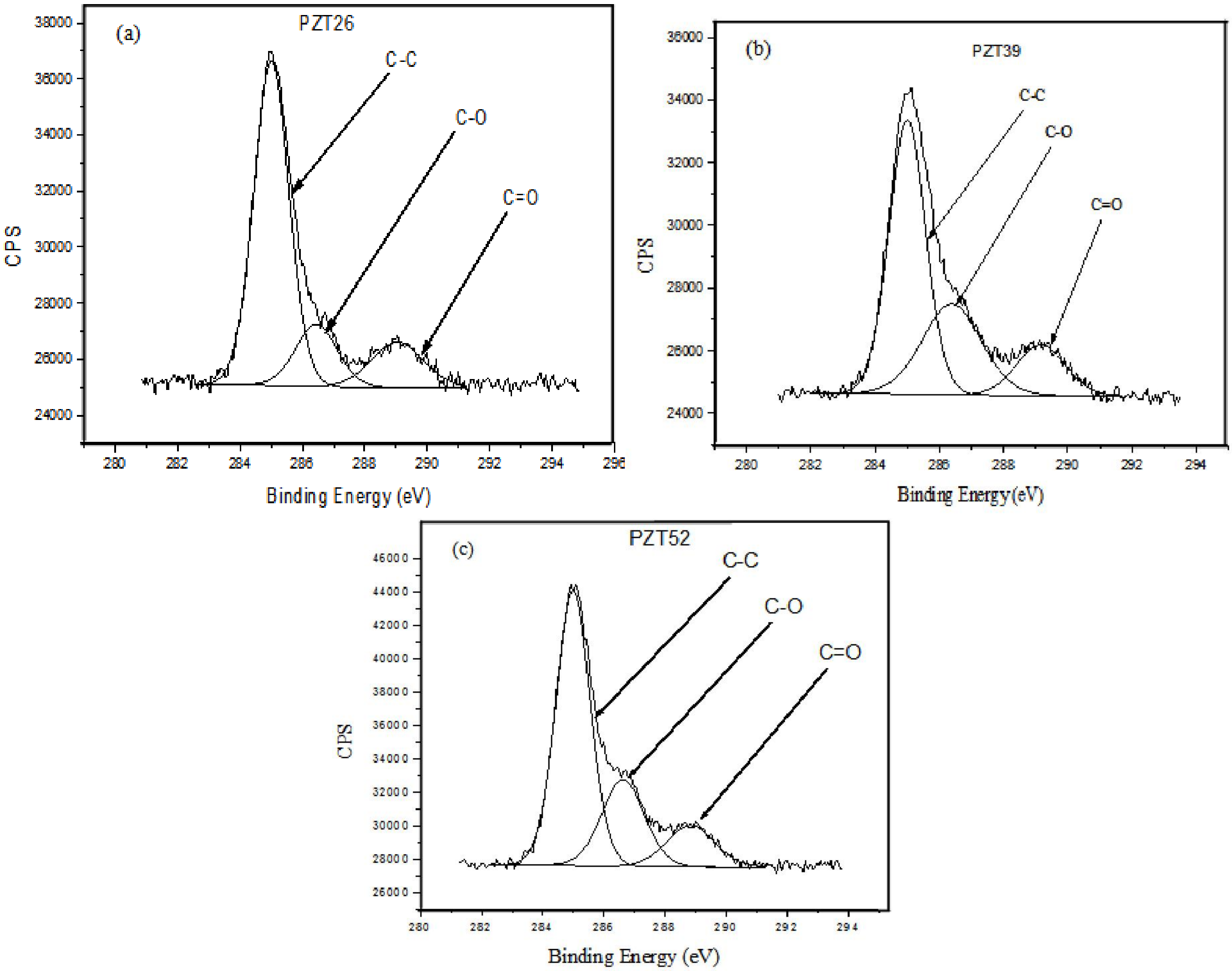
Table 2. Chemical Compositions of Zr and Ti Calculated and Extracted From Xps analysis

Calculated compositions	Compositions derived from XPS analyses
Pb $Zr_{0.26}Ti_{0.74}O_3$	Pb $Zr_{0.27}Ti_{0.73}O_3$
Pb $Zr_{0.39}Ti_{0.61}O_3$	Pb $Zr_{0.38}Ti_{0.62}O_3$
Pb $Zr_{0.52}Ti_{0.48}O_3$	Pb $Zr_{0.59}Ti_{0.41}O_3$
Pb $Zr_{0.65}Ti_{0.35}O_3$	Pb $Zr_{0.63}Ti_{0.37}O_3$
Pb $Zr_{0.78}Ti_{0.22}O_3$	Pb $Zr_{0.78}Ti_{0.22}O_3$

observed except for the composition with x=0.52 to which corresponds the value x= 0.59 estimated from XPS analysis. XPS Characterization also permits a qualitative analysis with the help of deconvolutions of the peaks present in the spectra. Each peak corresponds to a chemical element and deconvolution of these peaks allows knowing the corresponding chemical affiliation.

Table 1. Lattice parameters of the samples from the profile fit of XRD pattern

Elements	Sample 26	Sample 39	Sample 52	Sample 65	Sample 78
Al 2*s*	0,28	1,26	0,86	1,16	1,40
C 1*s*	14,62	16,52	22,92	16,25	16,13
Ca 3*s*	---	0,12	0,17	0,21	0,18
Cl 2*s*	---	0,45	---	0,27	0,54
O 1*s*	50,81	53,53	49,43	52,32	56,84
Pb 4*f*	19,01	14,20	12,75	15,04	15,64
Si 2*p*	2,23	3,79	5,56	7,43	---
Ti 2*p*	9,32	6,13	3,35	2,69	2,01
Zn 2*p*	0,24	0,18	0,26	0,16	0,07



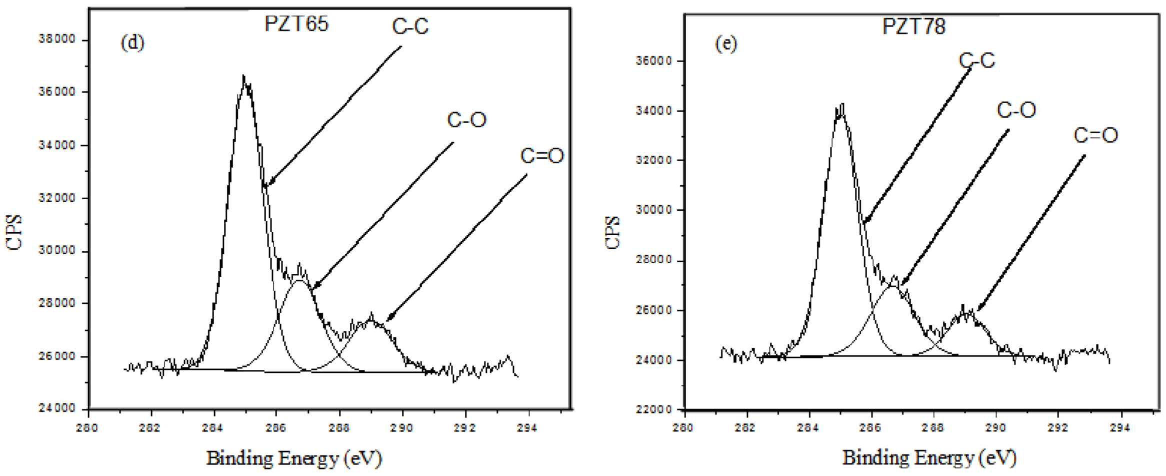


Figure 2. C1s peak deconvolution and chemical affiliations of C (a):PZT26,(b):PZT39,(c):PZT52,(d):PZT65,(e)PZT78

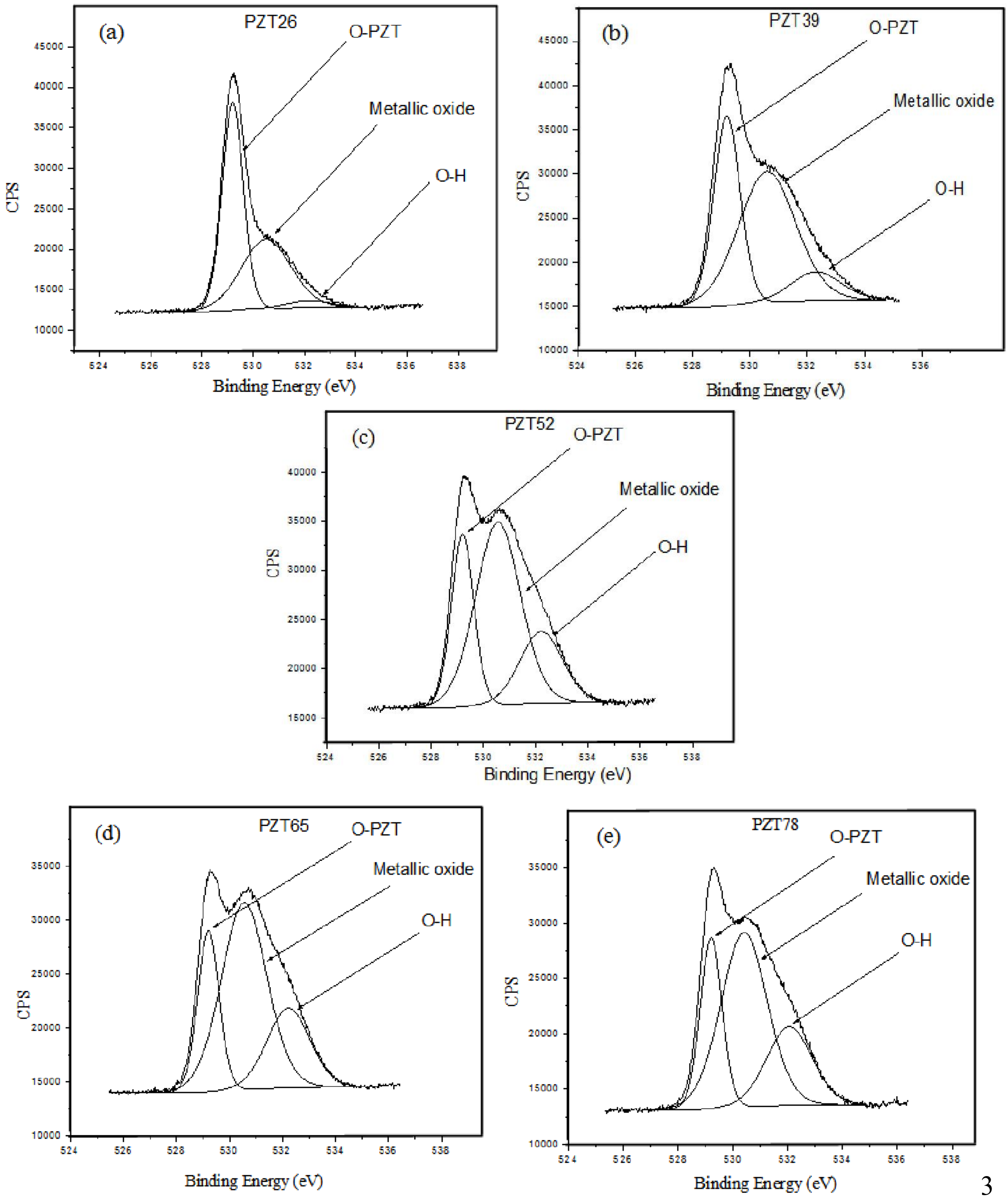


Figure 3. O1s peak deconvolution and chemical affiliations of O (a):PZT26,(b):PZT39,(c):PZT52,(d):PZT65,(e)PZT78

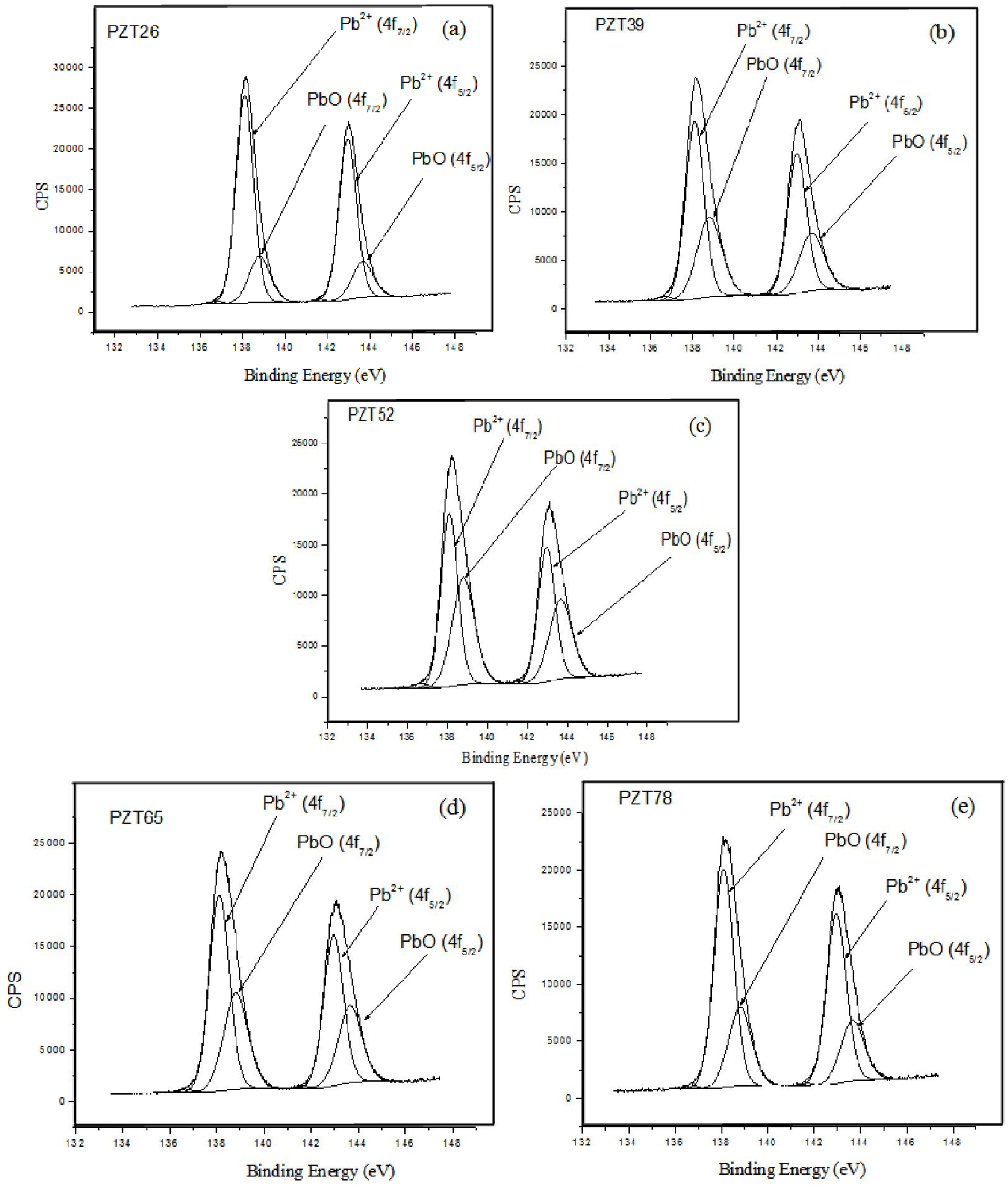
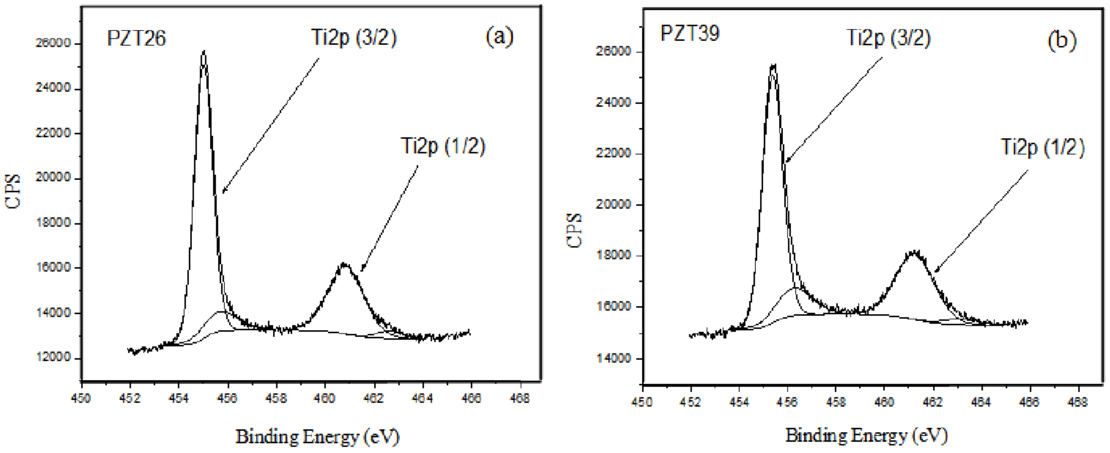


Figure 4. Pb4f peak deconvolution and chemical affiliations of Pb (a):PZT26,(b):PZT39,(c):PZT52,(d):PZT65,(e)PZT78



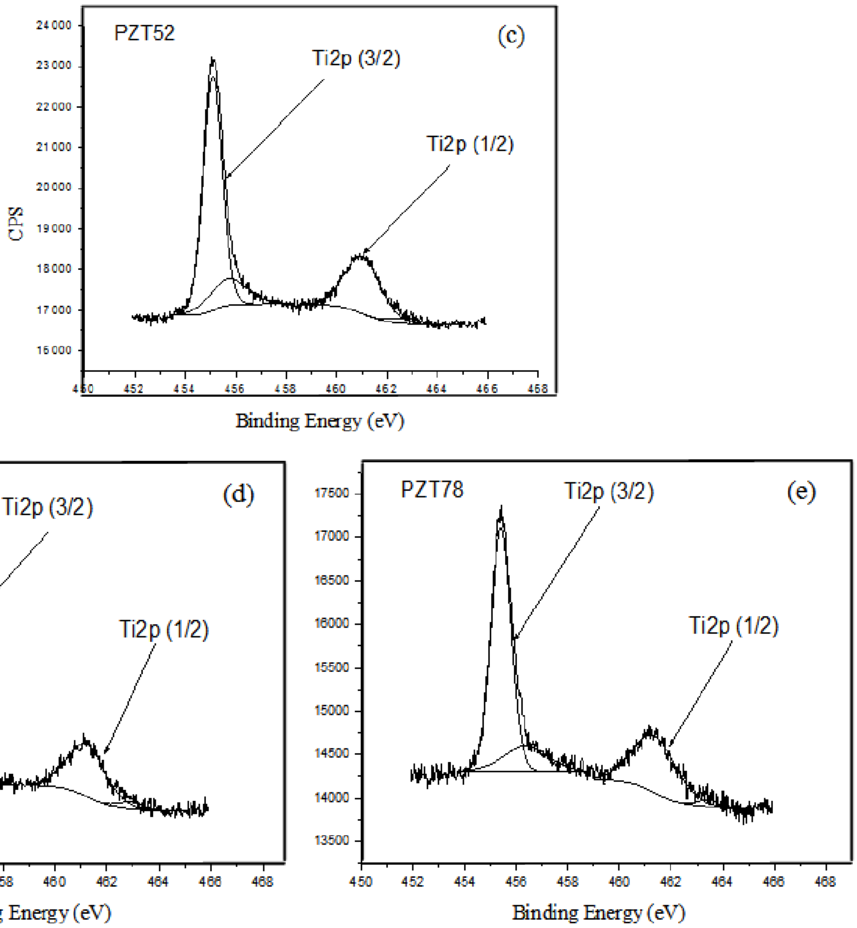


Figure 5. Ti2p peak deconvolution and chemical affiliations of Ti (a):PZT26,(b):PZT39,(c):PZT52,(d):PZT65,(e)PZT78

Table 3(a). Binding energies and chemical affiliations of C1s

Peak	Binding Energy (eV)					Chemical Affiliation	References
	26	39	52	65	78		
1	285,0	285,0	285,0	285,0	285,0	C–C/C–H	(Y Lin *et al.,* 2000 ; T J Zhu et L Lu, 2004)
2	286,4	286,4	286,6	286,7	286,7	C–O	(Y Lin *et al.,* 2000 ; T J Zhu et L Lu, 2004)
3	289,0	289,2	288,8	289,0	289,0	C=O	(Y Lin *et al.,* 2000)

Table 3(b). Binding energies and chemical affiliations of O1s

Peak	Binding Energy (eV)					Chemical Affiliation	References
	26	39	52	65	78		
1	529,2	529,2	529,2	529,2	529,2	O in PZT	(T J Zhu et L Lu, 2004 ; B D Qu *et al.,1992*)
2	530,5	530,6	530,6	530,5	530,4	metallic Oxides /O adsorbed	(T J Zhu et L Lu, 2004, N Wakiya *et al., 2000 ;* W C Hung *et al., 2008*)
3	532,2	532,3	532,2	532,2	532,0	–OH / organic contaminants	[Y Lin *et al.,* 2000 ; N Wakiya *et al.,2000 ;* G. Suchaneck *et al., 2009*)

Table 3(c). Binding energies and chemical affiliations of Pb 4f

Peak	Binding Energy (eV)					Chemical Affiliation	References
	26	39	52	65	78		
1	136,8	136,7	136,7	136,7	136,7	PbO (4f7/2) or charge effet	T J Zhu et L Lu, 2004 ; W L Chang and J L He,2004)
2	138,1	138,1	138,1	138,1	138,1	Pb2+ (4f7/2) (in PZT)	T J Zhu et L Lu, 2004 ; N. Wakiya *et al.,2000 ;* W L Chang and J L He,2004 ; J Wang *et al.,2004*)
3	138,8	138,8	138,8	138,8	138,8	PbO (4f7/2)	(W L Chang and J L He,2004; J N Kim *et al.,2003*; C H Park *et al.,2005*)
4	141,7	141,6	141,5	141,7	141,9	PbO (4f5/2) or charge effet	T J Zhu et L Lu, 2004 ; W L Chang and J L He, 2004)
5	143,0	143,0	143,1	142,9	143,0	Pb2+ (4f5/2) (in PZT)	T J Zhu et L Lu, 2004, N Wakiya *et al.,2000* ; J Wang *et al.,2004)*
6	143,7	143,7	143,7	143,6	143,7	PbO (4f5/2)	-

Table 3(d). Binding energies and chemical affiliations of Ti 2p

Peak	Binding Energy (without charge effect correction) (eV)				
	26	39	52	65	78
1	455,0	455,4	455,1	455,3	455,4
2	455,7	456,3	455,7	456,2	456,4
3	460,8	461,2	461,0	461,2	461,3
4	462,6	463,2	462,6	462,9	463,4

Table 3(e). Binding energies and chemical affiliations of Zr

Peak	Binding Energy (without charge effect correction) (eV)					Chemical Affiliation	References
	26	39	52	65	78		
1	181,3	181,3	181,3	181,3	181,3	Zr^{4+} ($3d_{5/2}$)	(T J Zhu et L Lu, 2004)
2	182,1	182,1	182,1	182,1	182,1	Zr–O (Zr $3d_{5/2}$)	(C I Lee *et al.,2009)*
3	183,7	183,6	183,7	183,7	183,7	Zr^{4+} ($3d_{3/2}$)	(T J Zhu et L Lu, 2004)
4	184,5	184,5	184,5	184,5	184,5	Zr–O (Zr $3d_{3/2}$)	(C I Lee *et al.,2009)*

Illustrations given in figures (Fig.2, Fig.3, Fig.4 and Fig.5) show chemical bonds contracted by Pb, O, Ti, Zr and C atoms. Tables 3(a), 3(b), 3(c), 3(d) and 3(e) gather binding energies of the samples together with their chemical affiliations.

Deconvolution of C1s peak (Fig.2) gives rise to the presence of three possible sub-peaks, corresponding to three bands C-C/C-H, C-O and C=O, located at about 285 eV, 286.5 eV and 289 eV, respectively. As carbon is not linked to other elements of PZT matrix, one may deduce that it is essentially present under the form of hydrocarbons which are adsorbed at the surface of the samples. On the other hand, as concentrations of Al, Ca, Cl, Si and Zn are relatively small (Table 1), they may be considered as pollutants at the surface of the samples, coming from the basic products or from used equipments; this is also the case of carbon even its concentration is relatively high. Concerning oxygen, the peak located around 529.2 eV may correspond to oxygens linked to the PZT matrix.

The peak located around 530.5 eV may be attributed to either metallic oxygen or to oxygen adsorbed at the surface of the samples, and the third peak around 532.2 eV may be considered as an O-H band; which implicates that this oxygen is an organic pollutant of the surface. Deconvolution of the peak Pb4f leads to a doublet: $Pb4f_{(7/2)}$ and $Pb4f_{(5/2)}$. The two peaks of this doublet are located at about 138.1 eV and 138.8 eV, respectively. They may be assigned to a $Pb4f_{(7/2)}$ in PZT and a $PbO4f_{(7/2)}$ band, respectively. The second doublet, located around 143 eV, may be seen as corresponding to a $Pb4f_{(5/2)}$ in PZT and a PbO $4f_{(5/2)}$ band.

In the case of Ti, the deconvolution spectrum shows the presence of Ti2p (3/2) and Ti2p (1/2) doublets. We have not given their chemical affiliations in Table (3d) as XPS analyses taken alone have not permitted such affiliations. Moreover, there exist numerous possibilities of affiliation cited in the literature (C Davoisne, 2006; B D Qu,1992; G Suchaneck, 2009). Table 3(e) gathers peaks positions (± 0,1 eV) together with their chemical affiliations. One can notice that Zr3d spectrum consists in a the doublet: Zr $3d_{5/2}$ and Zr $3d_{3/2}$.

Conclusion

XPS analyses have shown the presence of several contaminants at the surface of the samples. A good concordance has been found between nominal compositions of the species in the PZT matrix and those given by XPS analyses, which, in particular, indicates that PZT compositions are not affected by heat treatment during the annealing process.

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