

XPS STUDIES OF CERAMICS WITH PYROCHLOR STRUCTURE FOR RADIOACTIVE WASTES DISPOSAL

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ABSTRACT

X-ray photoelectron spectroscopy (XPS) study of ceramics $\text{CaThSn}_2\text{O}_7$ and $\text{CaThZr}_2\text{O}_7$ with pyrochlore structure used as matrixes for the disposal of long lived high level radioactive wastes was done. On the basis of the XPS parameters of the core and outer electrons in the binding energy range 0 - 1000 eV the oxidation states of the included metals were determined, quantitative elemental and ionic analysis was carried out and a conclusion on the monophaseness of the studied samples was drawn. The obtained data agree with the X-ray diffraction and scanning electron microscopy results.

Keywords: XPS, high-level wastes, ceramics.

Introduction

Processing of the irradiated spent fuel from the nuclear power plants produces a lot of radioactive wastes (RAW) including the high-level ones (HLW). The most dangerous HLW radionuclides are actinides and some long-lived decay products (^{93}Zr , ^{99}Tc , ^{126}Sn etc.). They are supposed to be included into the firm durable preservative matrixes for the subsequent underground disposal [1-3]. The correct choice of materials is the key problem of safety during the HLW processing. Understanding of the chemical processes in the matrixes requires a knowledge on the physical and chemical states of radionuclides and matrix elements. XPS proved to be the most adequate method for solution of this problem [4,5]. This work carried out the qualitative elemental and ionic analysis and studied the oxidation states of included elements for the two ceramics samples $\text{CaThZr}_2\text{O}_7$ and $\text{CaThSn}_2\text{O}_7$ with pyrochlore structure used as matrixes for the long-term storage of the HLW long-lived radionuclides.

Experimental

XPS spectra of the studied samples were measured with electrostatic spectrometers HP 5950A using monochromatized $\text{AlK}_{\alpha 1,2}$ ($h\nu=1486.6$ eV) radiation and MK II VG Scientific using non-

monochromatized $AlK_{\alpha 1,2}$ and MgK_{α} radiation under $1.3 \cdot 10^{-7}$ Pa at room temperature. The device resolutions were 0.8 eV (HP 5950A) and 1.2 eV (MK II VG Scientific). Electron binding energies were measured relatively to the binding energy of the C1s electrons from hydrocarbons absorbed on the sample surface accepted to be equal to 285.0 eV. The error in determination of electron binding energies were ± 0.2 eV and that of the relative line intensities was less than 10 %. The studied samples were prepared as pellets and as finely dispersed powders milled in the agate mortar pressed in indium on titanium substrate. For all the samples the quantitative elemental and ionic analysis was done by the following ratio: $n_i/n_j = (S_i/S_j)(k_j/k_i)$, where n_i/n_j – relative concentration of the studied atoms, S_i/S_j – relative core-shell spectral intensity, k_j/k_i – relative experimental sensitivity coefficient [6,7].

Results and discussion

Low binding energy (0 – 50 eV) XPS range. This spectral range for $CaThSn_2O_7$ (1) and $CaThZr_2O_7$ (2) exhibits the two-humped OVMO structures related to the outer valence $Ca4s, Th6d, 7s, Sn5s, 5p, Zr4d, 5s$ and $O2p$ electrons, as well as the IVMO structure due to the $Ca3s, 3p, Th6p_{3/2}, Sn4d, Zr4p$ and $O2s$ electrons (Fig.1, Table). Because of the high intense $Sn4d$ peak, the background on the higher binding energy side and the low calcium concentration, the $Ca3p$ and $Ca3s$ peaks at 24 and 43 eV respectively are not observed. These peaks are well observed in the XPS from $CaThZr_2O_7$ (2) exhibiting the $Zr4p$ peak instead of tin peaks (Fig. 1b). The $Th6p_{3/2}$ and $O2s$ peaks are well observed. Low intense peaks at 9 and 13 eV, apparently, must be attributed to the small amount of the CO_3^{2-} impurities on the sample surface. Their signature also presents in the C1s spectra.

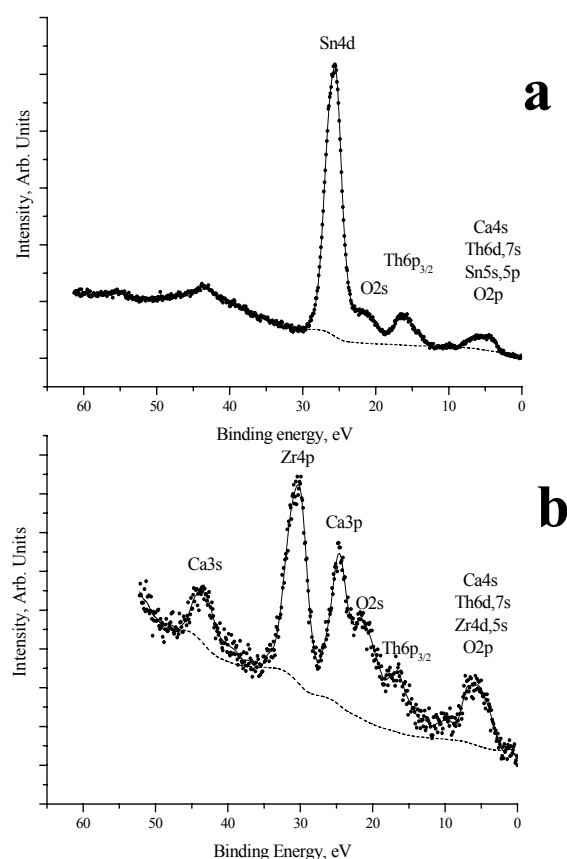


Fig. 1. Low binding energy XPS from: a - $CaThSn_2O_7$; b - $CaThZr_2O_7$.

Core electron (0 – 1000 eV) XPS structure. The most intense peaks are used for the XPS elemental and ionic quantitative analysis [6,7]. In the case of $\text{CaThSn}_2\text{O}_7$ (1) and $\text{CaThZr}_2\text{O}_7$ (2) they were: Ca2p, Th4f,5d, Sn3d, Zr3p,3d and O1s (Table). In case of overlap of the peaks close by the binding energies like Th4f – Zr3p for the Sample (2) (Fig.2b), the lower intense but most separate peaks like Th5d and Zr3d can be used. The Th4f and Ca2p peaks also somewhat overlap (Fig.2, Table). The Ca2p, Th4f, and Zr3p peaks appears as typical spin-orbit split doublets with ΔE_{sl} equal to 3.7 and 3.9 eV for the Ca2p, 9.3 and 9.5 eV for the Th4f in Samples (1) and (2) respectively. The considered XPS peaks were observed relatively sharp and single. It confirms the X-ray diffraction data on the high monophaseness of the considered samples. The Th4f_{7/2} spectrum from Sample (1) exhibits a shoulder on the lower binding energy side that can be attributed to the impurity (6%) of lesser oxidation state thorium (Fig.2a). The same shoulder (6%) appears in the Th5d_{5/2} spectrum from Sample (1) and does not appear in the spectra from Sample (2). The Sn3d and Zr3d spectra from Samples (1) and (2) appear as doublets also exhibiting shoulders on the lower binding energy sides (Fig.2). While in the Sn3d spectrum this shoulder is negligible, in the Zr3d one it reaches 7% intensity of the basic peak (Fig.2b).

Table. Binding energies E_b (eV) and FWHM Γ^a (eV) of the outer and core electrons for the pyrochlor ceramics.

Compound	MO	Th4f	Th5d	Zr3d Sn3d	Zr3p	Ca2p	O1s	C1s
$\text{CaThSn}_2\text{O}_7^b$ c)	5.1	334.6(1.1)	86.4(1.2)	486.9(1.3)		346.9	530.0(1.6)	285.0(1.3)
	16.3	343.9(1.1)	93.3(1.7)	495.3(1.2)		350.6	531.9	288.2
	21.2							
	25.8							
$\text{CaThZr}_2\text{O}_7^b$ c)	6.1	333.8(1.1)	86.4	181.6(1.1)	331.3	346.2	529.7(1.6)	285.0(1.3)
	16.6	343.3	93.3	183.9	341.3	350.1(2.0)	531.7	289.3
	21.5						532.9	
	24.6							
	30.2							
	34.3							
ThO ₂	5.8	334.3	86.3				530.2	285.0
	16.5	343.6	93.3					
	22.0							
	25.5							
CaZrO ₃ ^{d)}	5.3 20.6			181.7	332.3	350.3	529.8	285.0
	20.6			183.9			531.6	289.5
	24.8							
	30.0							
	43.6							
ZrO ₂	5.6 21.3			182.5	332.8		530.1	285.0
	30.6				346.4			
SnO ₂				486.7 495.1			530.6	285.0
Ca (металл)	-0.6 (1.2)					344.7(1.7)		285.0(1.3)
	23.4					348.4(1.7)		
	42.5(1.8)							
CaO	4.3 (2.1)					346.0(1.7)	528.9(1.4)	285.0(1.3)
	20.1 (2.6)					349.7(1.7)		
	24.3 (2.0)							

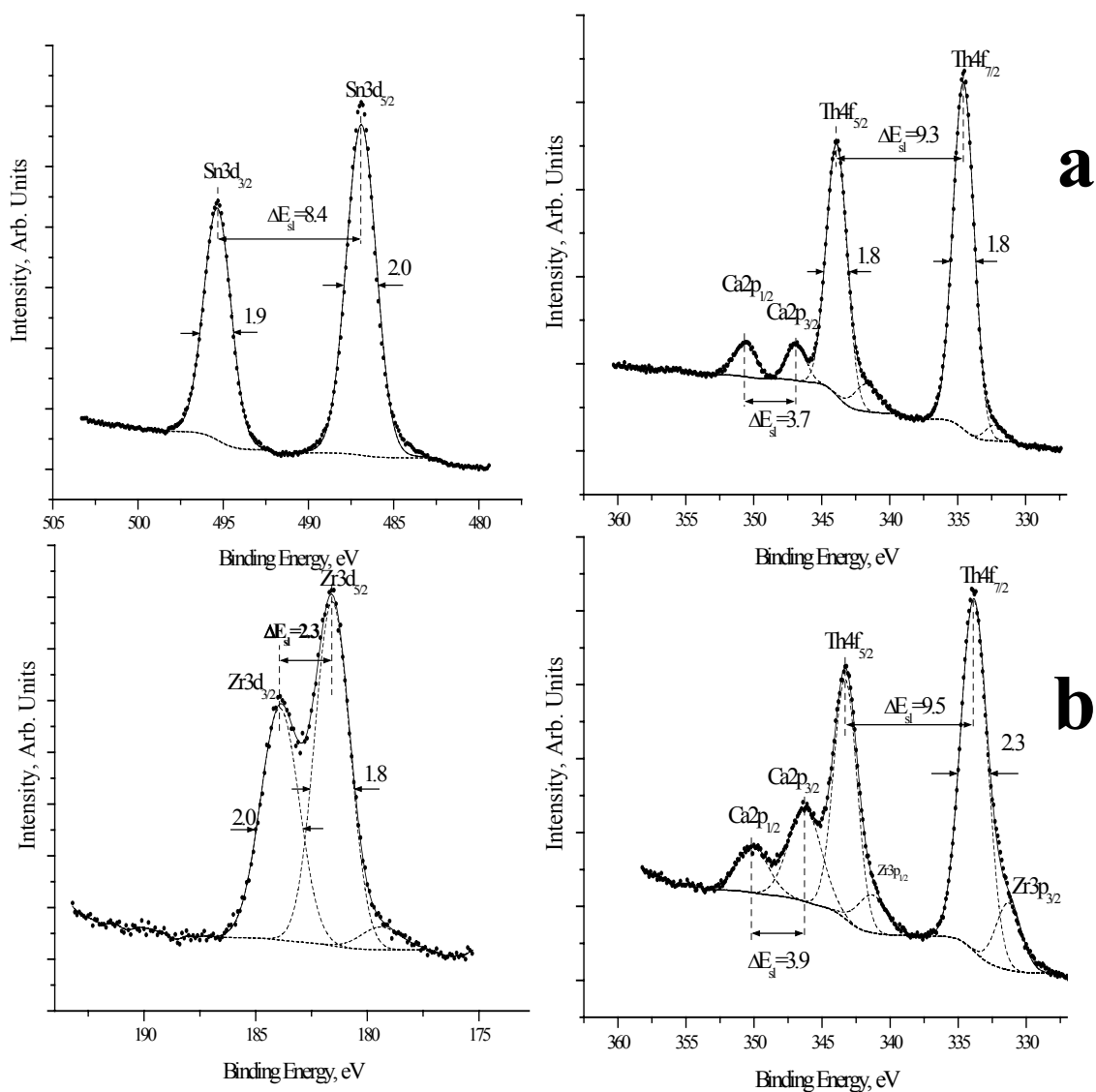


Fig.2. Core electron XPS: Th4f, Ca2p, Sn3d from CaThSn₂O₇ - a; and Th4f, Ca2p, Zr3d and Zr3p from CaThZr₂O₇ - b.

	42.9 (1.9)							
CaCO ₃	5.3 (2.2)					347.3(1.7)	531.6(1.6)	285.0(1.3)
	25.2 (2.0)					351.0(1.7)		289.7(1.3)
	44.1 (1.8)							

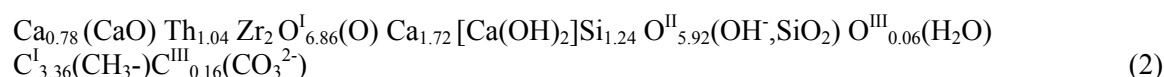
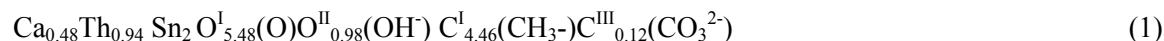
^a)FWHM relative to that of the C1s one 1.3 eV are given in parentheses.

^b)X-ray diffraction data: Ca_{0.92}Th_{0.92}Sn₂O_{6.96} (1) and Ca_{0.91}Th_{0.84}Zr_{2.25}O_{7.09} (2) [3].

^c)XPS data for the surface: Ca_{0.48}Th_{0.94}Sn₂O_{6.46} (1) and Ca_{2.50}Th_{1.04}Zr_{2.00}O_{12.84}(Si_{1.24}) (2), E_b(Si2p) = 102.8 eV.

^d)C1s and O1s binding energies for CO₃²⁻ group on the surface are marked.

Quantitative analysis results. The error increase in the quantitative elemental and ionic analysis of Samples (1, 2) can be explained by the extra XPS structure due to the multiplet splitting and secondary electronic processes (many-body perturbation and dynamic effect). The surfaces (~5 nm) of the studied samples were found to have the following composition relative to two atoms of tin (Sample 1) and one atom of zirconium (Sample 2):



where $\text{O}^{\text{I}}(\text{O})$, $\text{O}^{\text{II}}(\text{OH}^-)$, SiO_2 and $\text{O}^{\text{III}}(\text{H}_2\text{O})$ – oxygens of oxide, hydroxyl group and water. The surfaces of the studied samples can contain impurities of CO_3^{2-} groups, which can participate in formation of calcium carbonate. The obtained data slightly differ from the X-ray diffraction analysis results for the sample bulks:

$\text{Ca}_{0.48}\text{Th}_{0.94}\text{Sn}_2\text{O}_{6.46}$ (1) and $\text{Ca}_{2.50}\text{Th}_{1.04}\text{Zr}_{2.00}\text{O}_{12.84}(\text{Si}_{1.24})$ (2) - XPS data for the surface;

$\text{Ca}_{0.92}\text{Th}_{0.92}\text{Sn}_2\text{O}_{6.96}$ (1) and $\text{Ca}_{0.91}\text{Th}_{0.84}\text{Zr}_{2.25}\text{O}_{7.09}$ (2) – X-ray diffraction data for the bulk.

This difference can be explained by the fact that the XPS analysis reflects the surface (5-10 nm) composition. The XPS show that calcium on the surface of Sample 1 apparently presents as $\text{Ca}(\text{OH})_2$ and its surface concentration is twice lower than the bulk one.

Conclusions

1. X-ray photoelectron spectroscopy study of ceramics $\text{CaThSn}_2\text{O}_7$ and $\text{CaThZr}_2\text{O}_7$ with pyrochlore structure used as matrixes for the disposal of long lived high level radioactive wastes was done. The XPS proved to be an effective method for the elemental and ionic quantitative analysis of ceramics used as matrixes for the disposal of long lived high level radioactive wastes.
2. On the basis of the XPS parameters of the core and outer electrons in the binding energy range 0 - 1000 eV the oxidation states of the included metals were determined, quantitative elemental and ionic analysis was carried out and a conclusion on the monophaseness of the studied samples was drawn. The obtained data agree with the X-ray diffraction and scanning electron microscopy results.

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