THE XPS STUDY OF THE STRUCTURE OF URANIUM-CONTAINING CERAMICS

by

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The samples of the (Ca0.5GdU0.5)Zr2O7 and (Ca0.5GdU0.5)(ZrTi)O7 ceramics with the fluorite and pyrochlore structures used as matrices for the long-lived high-level radioactive waste disposal were studied with the X-ray photoelectron spectroscopy method. On the basis of the X-ray photoelectron spectroscopy parameters of the outer and core electrons from the binding energy range of 0-1250 eV the oxidation states of the included metal ions were determined, the quantitative elemental and ionic analysis was done, and the orderliness (monophaseness) was evaluated. The obtained data agree with the X-ray diffraction and the scanning electron microscopy results.

Key words: X-ray photoelectron spectroscopy, scanning electron microscopy, outer (OVMO) and inner (IVMO) valence molecular orbitals, pyrochlore, radioactive waste disposal

INTRODUCTION

The most dangerous long-lived radionuclides in the high-level radioactive waste (HLW) are actinides. Their immobilization requires the higher stability matrices. To understand the chemical processes inside these matrices it is necessary to know the physical and chemical states of the included radionuclides (elemental and ionic compositions, oxidation states, number of uncoupled electrons on the metal ions, close environment structure, etc.).

The correct choice of materials is the key problem of safety during the HLW management. Understanding of the chemical processes in the matrices requires knowledge of the physical and chemical states of the included radionuclides and matrix elements. It will allow a purposeful production of materials for the HLW and other wastes long-term storage [1-3].

The HLW containing actinides and some long-lived fission products (65Zr, 99Tc, 126Sn, etc.) are proposed to be included in the firm matrices for the later underground disposal. To understand the chemical processes inside these matrices it is necessary to know the physical and chemical states of the included matrix elements and radionuclides (elemental and ionic compositions, oxidation states, number of uncoupled electrons on the metal ions, close environment structure, etc.). The present work carried out an X-ray photoelectron spectral (XPS) study of the two ceramic samples (Ca0.5GdU0.5)Zr2O7 and (Ca0.5GdU0.5)(ZrTi)O7 with the fluorite and pyrochlore structures as possible matrices for the HLW disposal. Gadolinium (Gd) was introduced for neutron absorption. The XPS method has proven to be the most adequate for this purpose. On the basis of the core and outer electron XPS parameters in the binding energy range of 0-1000 eV the quantitative elemental and ionic analysis of the studied samples was done, oxidation states of the included metal ions were determined, and the interatomic metal-oxygen distances were evaluated.

The XPS proved to be an effective and adequate method for this field [4-6]. Therefore, this work carried out the qualitative elemental and ionic analysis and studied the oxidation states of included elements for the two ceramic samples (Ca0.5 GdU0.5)Zr2O7 (1) and (Ca0.5 GdU0.5)(ZrTi)O7 (2) with fluorite and pyrochlore structures used as matrices for the long-term storage of the long-lived radionuclides from HLW. Gadolinium was introduced in the matrices as a neutron absorber. The obtained results were compared with the X-ray diffraction and scanning electron microscopy data.

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EXPERIMENTAL

Samples with the calculated compositions (Ca_{0.5}GdU_{0.5})Zr_{2}O_{7} (1) and (Ca_{0.5}GdU_{0.5})(ZrTi)O_{2} (2) were prepared from the mixtures of CaCO_{3}, Gd_{2}O_{3}, UO_{2}, TiO_{2}, and ZrO_{2} ground in an agate mortar to the size of 20 µm to 30 µm. The mixtures were pressed under 200 MPa to 400 MPa into 12 mm to 30 mm diameter 4 mm to 5 mm high cylindrical pellets and sintered in alundum crucibles at 1500 °C-1550 °C for 6 hours to 10 hours. The structure of pyrochlore samples was studied with XRD on the DRON-4 (CuKα), as well as on the scanning (SEM/EDS: JSM-5300 with the energy-dispersion spectrometer Link ISIS) and transmission (JEM-100) electron microscopes [3-5].

XPS spectra of the studied samples were measured with electrostatic spectrometers HP 5950A using monochromatized AlK_{α1,2} (hν = 1486.6 eV) radiation and MK II VG Scientific using non-monochromatized AlK_{α1,2} and MgK_{α} radiation under 1.3·10^{-7} Pa at room temperature. The device resolutions measured as full width at the half-maximum (FWHM) of the Au4f_{7/2} peak on the standard rectangular gold plate were 0.8 eV (HP 5950A) and 1.2 eV (MK II VG Scientific). Electron binding energies E_{0j}(eV) 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. For the gold standard the calibration binding energies E_{0j}(C1s) = 285.0 eV and E_{0j}(Au4f_{7/2}) = 83.7 eV (MK II VG Scientific) were used. The FWHM in tab. 1 are given relatively to that of the C1s peak of hydrocarbons accepted to be equal to 1.3 eV for comparison with the data of other studies [4-6]. The uncertainty in determination of electron binding energies was ±0.2 eV and that of the relative peak intensities was less than 10%. The studied samples were prepared as pellets (samples 1 and 2) and as finely dispersed powders ground in an agate mortar pressed in indium on titanium substrate (standard samples).

The quantitative elemental and ionic analysis was done for all the samples. It was based on the fact that the spectral intensity is proportional to the number of certain atoms in the studied sample. The following ratio was used: \( n_{i}/n_{j} = (S_{i}/S_{j})(k_{i}/k_{j}) \), where \( n_{i}/n_{j} \) is the relative concentration of the studied atoms, \( S_{i}/S_{j} \) – the relative core-shell spectral intensity, and \( k_{i}/k_{j} \) – the relative experimental sensitivity coefficient. This work used the following coefficients relative to carbon: 1.00 (C1s); 2.66 (O1s); 4.2 (Ca2p), 6.32 (Ca2p); 8.4 (Zr3d), 4.16 (Zr3p3/2), 36.0 (U4f7/2), 1.08 (Si2p) [7, 8]. XPS parameters of Ca, CaO, CaCO_{3}, UO_{2}, SnO_{2}, ZrO_{2}, and SrZrO_{3} (tab. 1) were used for the interpretation of the spectra from the studied samples.

RESULTS AND DISCUSSION

The XPS from the studied HLW matrixes ceramics (Ca_{0.5}GdU_{0.5})Zr_{2}O_{7} (sample 1) and (Ca_{0.5}GdU_{0.5})(ZrTi)O_{2} (sample 2) – in the binding energy range of 0-1250 eV exhibit the peaks attributed to the included elements (fig. 1). This binding energy range can be subdivided into the three sub-ranges [4-6]. The first one from 0 to ~15 eV exhibits the structure attributed mainly to the electrons of the outer valence molecular orbitals (OVMO) formed with electrons from incompletely filled atomic valence shells. For example, the An5f intensity at zero binding energy can be used for determination of actinide oxidation states [4]. The second binding energy sub-range from ~15 eV to ~50 eV exhibits the structure attributed to the electrons of the inner valence molecular orbitals (IVMO) formed with electrons from the completely filled atomic low-energy shells. Parameters of this structure characterize the close environment of the considered ion, in particular, for actinide com-

Figure 1. Survey XPS in the binding energy range of 0-1250 eV from samples: (a) – (Ca_{0.5}GdU_{0.5})Zr_{2}O_{7}; (b) – (Ca_{0.5}GdU_{0.5})(ZrTi)O_{2}
pounds the IVMO parameters can be used for determination of the actinide-neighbour interatomic distance [6]. The third sub-range above ~50 eV shows the structure attributed to the core electronic shells weakly participating in the chemical bonding. However, this sub-range can exhibit the structure due to the spin-orbit splitting $\Delta E_{\text{sl}}$(eV), multiplet splitting $\Delta E_{\text{ms}}$(eV), many-body perturbation, dynamic effect, etc. [4, 5]. Since these structure parameters correlate with the physical and chemical properties of compounds, they are used together with the traditional XPS characteristics like electron binding energies, chemical shifts, core-valence binding energy differences, and peak intensities [7, 8]. To simplify the discussion, we are going to use both molecular and atomic terms.

**Low binding energy XPS (0 to ~50 eV).** The low-binding energy XPS range from (Ca$_{0.5}$GdU$_{0.5}$)$_2$Zr$_2$O$_7$ (1) and (Ca$_{0.5}$GdU$_{0.5}$)(ZrTi)O$_7$ (2) exhibit the two-humped OVMO structures attributed to the outer valence Ca4s, U5f,6d,7s, Zr4d,5s, Gd4f,5d,6s, Ti3d,4s, and O2p electrons, as well as the IVMO structure due to the Ca3s,3p, U6p, Gd5p,5s, Zr4p, Ti3p, and O2s electrons (fig. 2, tab. 1). The Zr4p, O2s, and other peaks are observed to be sharp. This XPS structure allows only a qualitative elemental analysis because the considered spectra appear as complicated MO-related lines, not single peaks. This binding energy range consists of only the peaks attributed to the included elements. Small peaks at 9 eV and 13 eV can be explained by the presence of a CO$_2^-$ impurity on the sample surface, which was confirmed by the Cls spectra.

**Core-electron XPS (~50 eV to 1250 eV).** The XPS elemental and ionic quantitative analysis usually employs the most intense peaks from the included elements [7, 8]. In the case of the studied compounds (Ca$_{0.5}$GdU$_{0.5}$)$_2$Zr$_2$O$_7$ (1) and (Ca$_{0.5}$GdU$_{0.5}$)(ZrTi)O$_7$ (2) the Ca2p, U4f, Gd3d$_{5/2}$, 4d, Zr3p,3d, Ti2p, and O1s peaks were used (tab. 1). In the case of an overlap of the peaks, other available single peaks like, for instance, the Th5d and Zr3d can be used. The Cls XPS from the samples (1) and (2) were observed to be symmetrical with the low-intense shoulders of the CO$_2^-$ groups at 289.1 eV and 287.3 eV (tab. 1). A small widening of the Cls peak from the sample (2) in comparison with that from the sample (1) can be explained by the inhomogeneous charging of the sample surface or by the presence of hydrocarbons of different types on the surface.

The Zr3p and Ca2p peaks overlap (fig. 3, tab. 1). The Ca2p and Zr3p are observed as typical spin-orbit split ($\Delta E_{\text{sl}}$(Ca2p) = 3.7 eV, $\Delta E_{\text{sl}}$(Zr3p) = 13.6 eV) doublets [9]. The Zr3d XPS from the samples (1) and (2) appear as symmetrical doublets. The U4f XPS are also observed as spin-orbit split doublets typical for the U(IV) ions shake-up satellites (fig. 4). The peaks from the included elements were observed to be single and sharp. It confirms the XRD results that the considered samples are monophase (figs. 3 and 4). The Gd4d XPS show the fine structure typical for the Gd(III) ions (tab. 1). But, for the studied samples (1 and 2) these spectra exhibit an extra peak at 152.6 eV that must be attributed to the Si2s peak from the silicon impurity. The Gd3d$_{5/2}$ XPS correspond to Gd(III) in Gd$_2$O$_3$ (tab. 1). These spectra show extra peaks at 1196.1 eV which are attributed to the CaKLL Auger spectra (1195.6 eV). The Ti2p XPS appears as a spin-orbit split doublet ($\Delta E_{\text{sl}} = 5.8$ eV) and shake-up satellites.

The O1s XPS from the sample (1) consists of the three peaks at 529.0, 530.5, and 531.6 eV, and that from the sample (2) consists of the three peaks at 529.2 eV, 530.9 eV, and 532.1 eV (fig. 5). Taking into account eqs. (I, II) from [10]

$$E_b = 2.27 \frac{R_{\text{M-O}^{-1}}}{(\text{nm})} + 519.4 \quad \text{(I)}$$

where

$$R_{\text{M-O}}(\text{nm}) = 2.27 (E_b - 519.4)^{-1} \quad \text{(II)}$$

![Figure 2. Low binding energy XPS from samples:](image-url)
On the basis of the O1s binding energies one can evaluate the metal-oxygen interatomic distances $R_{M-O}$ (nm) in the samples (1) and (2). Thus, for the sample (1) they are 0.236 nm, 0.205 nm and 0.186 nm, respectively, while for the sample (2) – 0.232 nm, 0.197 nm, and 0.179 nm, respectively. Since the O1s binding energy can be measured with the accuracy to within ±0.05 eV, not ±0.2 eV as it was measured in this work, the accuracy of the interatomic distance evaluation can be higher. As it follows from eq. (1) as the interatomic distance $R_{M-O}$ grows, the O1s binding energy decreases. Therefore, one can conclude that, for example, the value 0.179 nm is too low to be observed in ceramics. Apparently, this distance can be attributed to a surface state.

The two low-energy O1s components in the XPS from the samples (1 and 2) can be attributed to the oxides of the basic ceramics, but the higher-energy components are, apparently, attributed to impurities like Ca(OH)$_2$, SiO$_2$, CO$_3^{2-}$, Na$_2$O, etc. (fig. 5, tab. 1). It has to be noted that, for example, in ZrO$_2$ three oxygens are located from zirconium at 0.207 nm, four oxygens – at 0.221 nm, and the next closest oxygen not belonging to the first co-ordinating sphere – at 0.358 nm [11]. For this environment the O1s XPS must consist of two peaks at 530.4 eV and 529.7 eV with the intensity ratio 4/3. Therefore, the interatomic distances evaluated on the basis of the O1s XPS are good enough for the qualitative and partially quantitative identification of the O1s XPS peaks.

**Quantitative analysis.** The uncertainty in the quantitative elemental analysis of the samples 1 and 2 increases because the core XPS peaks have the multiplet splitting and secondary electronic processes related extra structure. Since the many-body perturbation results in the shake-up satellites on the higher binding energy side from the basic peaks, their intensities can be taken into account (fig. 4). The dynamic ef-

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**Table 1. Binding energies $E_b$ (eV) and FWHM $\Gamma^{(a)}$ (eV) of the outer and core electrons from pyrochlore ceramics**

<table>
<thead>
<tr>
<th>Compound</th>
<th>MO</th>
<th>An4f Ln3d</th>
<th>An5d Ln4d</th>
<th>Zr3d Sn3d</th>
<th>Zr3p</th>
<th>Ca2p</th>
<th>Ti2p</th>
<th>O1s</th>
<th>C1s</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Ca$<em>{0.5}$Gd$</em>{0.5}$)Zr$_2$O$_7$</td>
<td>7.0</td>
<td>20.3</td>
<td>25.0</td>
<td>29.5</td>
<td>43.7</td>
<td>380.7</td>
<td>391.4</td>
<td>1186.7</td>
<td>140.4</td>
</tr>
<tr>
<td>(Ca$<em>{0.5}$Gd$</em>{0.5}$)(ZrTi)O$_7$</td>
<td>7.2</td>
<td>23.7</td>
<td>29.5</td>
<td>36.0</td>
<td>42.5</td>
<td>380.4</td>
<td>391.2</td>
<td>1186.3</td>
<td>140.2</td>
</tr>
<tr>
<td>UO$_2$</td>
<td>1.9</td>
<td>6.1</td>
<td>20.8</td>
<td>23.3</td>
<td>380.9</td>
<td>391.8</td>
<td>97.3</td>
<td>105.5</td>
<td>45</td>
</tr>
<tr>
<td>CaZrO$_3$</td>
<td>5.3</td>
<td>20.6</td>
<td>20.6</td>
<td>24.8</td>
<td>30.0</td>
<td>43.6</td>
<td></td>
<td></td>
<td>181.7</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>5.6</td>
<td>21.3</td>
<td>30.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>182.5</td>
</tr>
<tr>
<td>Ca (metal)</td>
<td>–0.6</td>
<td>(1.2)</td>
<td>23.4</td>
<td>42.5</td>
<td>(1.8)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>4.3</td>
<td>(2.1)</td>
<td>20.1</td>
<td>(2.6)</td>
<td>24.3</td>
<td>(2.0)</td>
<td>42.9</td>
<td>(1.9)</td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>5.3</td>
<td>(2.2)</td>
<td>25.2</td>
<td>(2.0)</td>
<td>44.1</td>
<td>(1.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>5.9</td>
<td>7.6</td>
<td>22.4</td>
<td>37.4</td>
<td>62.6</td>
<td>3s</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gd$_2$O$_3$</td>
<td>5.7</td>
<td>9.0</td>
<td>22.3</td>
<td>27.4</td>
<td></td>
<td>1187.3</td>
<td>1219.3</td>
<td>142.8</td>
<td>147.9</td>
</tr>
</tbody>
</table>

(a)FWHM are given in parentheses relative to the FWHM of the C1s, $\Gamma(C1s) = 1.3$ eV;
(b)O1s and C1s binding energies (531.6 and 289.5 eV) for the CO$_3^{2-}$ group on the surface.
fect is more difficult to take into account, but its influence is low. All these effects lead to an enhancement of the uncertainty in the elemental and ionic quantitative analysis, so the total uncertainty can exceed 10%. In this approximation the surface (~5 nm) compositions of the studied samples relative to zirconium atoms were found to be

$$\text{(Ca}_{0.50}\text{Gd}_{1.14}\text{U}_{0.42})\text{Zr}_{2.00}\text{O}_{6.18}\text{O}^{I}_{1.88}\text{O}^{II}_{9.90}\text{O}^{III}_{6.08}\text{Si}_{2.82}(\text{CH}_{3})\text{C}^{0.82}(\text{CO}_{3})\text{O}^{2-}\text{(1)}$$

$$\text{(Ca}_{0.50}\text{Gd}_{1.00}\text{Ti}_{1.37})\text{Zr}_{2.00}\text{O}_{6.18}\text{O}^{I}_{1.88}\text{O}^{II}_{9.90}\text{O}^{III}_{6.08}\text{Si}_{2.82}(\text{CH}_{3})\text{C}^{0.82}(\text{CO}_{3})\text{O}^{2-}\text{(2)}$$

where $\text{O}^{I}(O)$, $\text{O}^{II}(O)$, and $\text{O}^{III}(OH^{-}, \text{SiO}_{2})$ are oxygens of oxides and hydroxyl groups (silicon dioxide). In the studied samples the $\text{CO}_{3}^{2-}$ impurities from calcium carbonate are present on the surface.

The obtained data differs slightly from the XRD results measured for the sample bulk.

Figure 3. Zr3p and Ca2p XPS from samples:
(a) – (Ca$_{0.5}$Gd$_{1.14}$U$_{0.42}$)Zr$_{2}$O$_{7}$; (b) – (Ca$_{0.5}$Gd$_{1.0}$Ti$_{1.37}$)Zr$_{2}$O$_{7}$

Figure 4. U4f XPS from samples:
(a) – (Ca$_{0.5}$Gd$_{1.14}$U$_{0.42}$)Zr$_{2}$O$_{7}$; (b) – (Ca$_{0.5}$Gd$_{1.0}$Ti$_{1.37}$)Zr$_{2}$O$_{7}$

It can be explained by the fact that the XPS reflects the 5 nm to 10 nm surface composition, while the XRD reflects the bulk. The XPS shows that calcium on the surface of the studied samples (1) and (2) is present partially in form of hydroxide, and it gathers more preferably on the surface rather than in the bulk. The relative surface and bulk titanium, zirconium, and uranium contents do not differ significantly. During the study of the Bi-Ca-Cu-O-based metal-oxide ceramics [12] it was found that calcium hydroxides and carbonates are formed on the sample surface under the environment influence. In other words, the instability of the ceramic surface is associated with the presence of calcium oxides.
CONCLUSIONS

On the basis of the core and outer electrons XPS parameters of the studied ceramics \((\text{Ca}_{0.5}\text{GdU}_{0.5})\text{Zr}_2\text{O}_7\) and \((\text{Ca}_{0.5}\text{GdU}_{0.5})\text{(ZrTi)}\text{O}_7\) in the binding energy range of 0-1250 eV the oxidation states of the included metals were determined, quantitative elemental and ionic analysis was carried out and a conclusion on the monophaseness (orderliness) of the studied samples was drawn. The obtained data agree with the X-ray diffraction and scanning electron microscopy results. It is shown that the XPS method can be effectively applied for the study of the elemental and ionic composition of ceramic matrices for the HLW disposal.

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ПРОУЧАВАЊЕ СТРУКТУРЕ КЕРАМИКА СА САДРЖАЈЕМ УРАНИЈУМА РЕНДГЕН-ИНДУКОВАНОМ СПЕКТРОСКОПИЈОМ

Узорци керамике флуоритне и пирохлорне структуре, \((Ca_{0.5}Gd_{0.5})Zr_2O_7\) и \((Ca_{0.5}Gd_{0.5})(ZrTi)O_7\), који су коришћени као матрици за радиоактивни отпад са дугоживећим радионуклидима високог нивоа активности, проучавани су методом рендген-индуковане фотоелектронске спектроскопије. На основу спектроскопских параметара електрона у језгру и у електронском омотачу, у опсегу енергије веза од 0 eV до 1250 eV, одређена су оксидациона стања присутних металних јона, урађена је квантитативна анализа елемената и јона и процењена је монофазност. Постигнути резултати су у сагласности са резултатима добијеним помоћу рендгенске дифракције и скенирајуће електронске микроскопије.

Кључне речи: рендген-индукована спектроскопија, скенирајућа електронска микроскопија, молекуларне валентне орбите, пирохлор, одлагање радиоактивног отпада