X-Ray Photoelectron Spectroscopy of Murataite Ceramics Containing Lanthanides

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Abstract—Ceramic samples with the following composition (wt %): 50 TiO₂, 10 CaO, 10 MnO₂, 5 Al₂O₃, 5 Fe₂O₃, 10 ZrO₂, 10 Ln₂O₃ (Ln = La, Ce, Nd, Ho) or 10 CeO₂, were studied by X-ray photoelectron spectroscopy. According to the data of X-ray phase analysis and scanning electron microscopy, they consist of murataite, zirconolite, and perovskite. In smaller quantities there are crichtonite, pyrophanite-ilmenite, and rutile. Ce³⁺ dominates in cerium samples: the Ce³⁺ : Ce⁴⁺ ratio is 3 : 1 and does not depend on the method of adding the element to the charge—in the form of CeO₂ or Ce₂O₃. All ceramics are dominated by Fe³⁺, its fraction is 92–94 rel %, while manganese is represented only by Mn³⁺ cations.

Keywords: lanthanides, ceramics, murataite, valency, XPS

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INTRODUCTION

High-level waste (HLW) from nuclear power and military activities is vitrified for subsequent placement in underground storage facilities [1–5]. Glasses do not fully meet the requirements for waste matrices in terms of safety and economy. Their capacity for waste is rather low, especially that of aluminophosphate glasses [1, 6], which reduces the efficiency of using the underground HLW storage. When such matrices come into contact with water, colloidal particles that can migrate in the geological environment are formed. Glasses are metastable formations and will crystallize over time, which will cause an increase in the leaching rate of radionuclides due to the appearance of soluble newly formed phases [7]. In the future, it is planned to employ new technologies for reprocessing spent nuclear fuel (SNF), including the separation of HLW into groups of elements [3]. This fact makes it relevant to search new matrices for the immobilization of actinides, for example, crystalline materials based on titanates and zirconates

[2–5, 8–10]. Such promising matrices of actinides and rare-earth elements (REE) actinides include, in particular [10, 11], pyrochlore-based ceramics (double fluorite cell, Py)—muratite (triple fluorite cell, M3) with intermediate members M5 and M8 (murataites with a five- or eight-fold fluorite unit cell). Upon crystallization from the melt, they are formed in the sequence: Py → M5 → M8 → M3 with the formation of zoned grains with a maximum concentration of actinides and rare earths in their central part [3, 11].

Light lanthanides of the cerium group (La, Ce, Nd, Sm, Pr) dominate in the REE-actinide fraction and also serve as imitators of actinides in the corresponding oxidation states: La³⁺ and Nd³⁺ for Am³⁺ and Cm³⁺, Ce^{3+/4+} for Pu^{3+/4+}. Therefore, data on the oxidation state of lanthanides in ceramics are of scientific and practical interest. The method of X-ray photoelectron spectroscopy (XPS) makes it possible to determine the elemental and ionic composition of the surface of the samples [12–17]. Previously, this method was

Fig. 1. SEM image of La (a: (1) murataite, (2) perovskite, (3) zirconolite, (4) crichtonite), Nd (b: (1, 2) murataite; (3) perovskite; (4) zirconolite; (5) crichtonite), Ce3 (c: (1) zirconolite, (2,3) murataite, (4) perovskite), Ce4 (d (1,2) murataite, (3) perovskite, (4) crichtonite). Scale marks are equal to (a, c) 100, (b) 20, and (d) 50 μm .

used to analyze Ln and An-containing glasses and ceramics [18–22], including those based on murataite. No information has been found in the literature on the XPS study of ceramics containing La, Ce, Nd, and Ho. We have studied ceramics samples with La, Ce, Nd, or Ho to determine the surface composition and predict their behavior during long-term storage and disposal. These elements were chosen due to the fact that La, Ce, and Nd dominate among the fission products in HLW. In addition, Ce in oxidation states III and IV serves as an imitator of actinides, for example, Pu(III) and Pu(IV). Holmium was introduced to study the effect of an element cation radius on the phase composition of ceramics with REE.

EXPERIMENTAL

The samples were synthesized in a VTP-12/15 furnace by melting mixtures of the following composition (wt %): 50 TiO_2 , 10 CaO , 10 MnO_2 , 5 Al_2O_3 , 5 Fe_2O_3 , 10 ZrO_2 , 10 Ln_2O_3 ($\text{Ln} = \text{La, Ce, Nd, Ho}$) or 10 CeO_2 in glassy carbon crucibles at 1500°C for 0.5 h and cooling after the furnace turning off. They were studied by X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDX); some of the results are reported in [23]. XPS spectra were recorded on a Kratos Axis Ultra DLD instrument using monochromatic AlK_α radiation ($h\nu = 1486.7 \text{ eV}$) from $300 \times 700 \mu\text{m}$ areas, which is tens of times larger than the grain size of the ceramics phases. To prepare an unoxidized surface, the samples were

cleaved and immediately placed into the spectrometer. Binding energies (E_b) are measured relative to E_b of C 1s electrons of hydrocarbons on the sample surface equal to 285.0 eV. The error in determining the binding energy and line width is less than $\pm 0.05 \text{ eV}$, the error in determining the peak intensity is not higher than $\pm 5\%$. The background associated with secondary scattered electrons was subtracted by the Shirley method [24]. The composition was analyzed according to the method described in [25] to a depth of 10 nm [26, 27].

RESULTS AND DISCUSSION

The structure of the samples is shown in Fig. 1, the relative amount and composition of the phases, in Tables 1 and 2. Lanthanides are distributed among murataite, zirconolite, perovskite, crichtonite. In the samples of La, Ce3, Ce4, and Nd, their highest concentrations are observed in perovskite therewith in the sample of Ce4 there are two types: with a low and high cerium content. The phase composition of ceramics with cerium is somewhat different: the Ce3 sample contains less amount of murataite and there is zirconolite. With a decrease in the radius of the Ln ion the amount of perovskite decreases and it is absent in the holmium sample. In the sample with holmium, the highest Ho content is observed in zirconolite. The main Ln concentrator in ceramics is murataite (all its modifications M5, M8, and M3), except for the La sample with the highest amount of perovskite.

The spectra of Ln ions in ceramics are a combination of their spectra in separate phases. The survey spectra of the samples contain lines of all elements, as well as Auger spectra of carbon (C *KLL*), oxygen (O *KLL*), and iron (Fe *LMM*) (Fig. 2). They can be divided into two parts: the low energy region (from 0 to 50 eV) of valence electrons and the region of core electrons (above 50 eV). Consider the structure of these regions in more detail.

The region of valence electrons. In the spectral range from 0 to 15 eV the lines of outer electrons (OVMO) and in the range from 15 to 50 eV, of inner valence molecular orbitals (IVMO) are observed (Figs. 2a–2d, Table 3). The electron spectrum of the OVMO contains a number of peaks, but does not provide information on the sample composition. A weak maximum at 1.7 eV (Fig. 3a) is associated with the Ce 4f electrons, which do not participate in the chemical bonding of Ce^{3+} ions [28]. The lines of Ca 3s-, Mn 3p-, Zr 4s-, and O 2s-electrons are observed: their intensity can be used for qualitative and quantitative elemental analysis.

Table 1. Target composition of the samples and the phases identified in them. XRD and SEM/EDS data

Sample	Component content, wt %							Phases and their ratio according to XRF and SEM/EDS data ^a
	Al ₂ O ₃	CaO	TiO ₂	MnO	Fe ₂ O ₃	ZrO ₂	Ln ₂ O ₃	
La	5	10	50	10	5	10	10	Z ~ M ~ P > C >> P/I > R
Ce3	5	10	50	10	5	10	10 (Ce ₂ O ₃)	Z > P ~ M > C
Ce4	5	10	50	10	5	10	10 (CeO ₂)	M > P > C > P/I
Nd	5	10	50	10	5	10	10	M > Z ~ P > C
Ho	5	10	50	10	5	10	10	M > Z > C

^a (M) murataite (all modifications), (P) perovskite, (Z) zirconolite, (C) crichtonite, (P/I) pyrophanite/ilmenite, (R) rutile.

Table 2. Phase formulas in ceramic samples with lanthanides, SEM/EDS analysis data^a

Sample	Phase	Formulas calculated based on the charge of cations: Ce ³⁺ , Fe ³⁺ and Mn ³⁺
La	Zirconolite	[(Ca _{0.46} La _{0.03})Zr _{0.81} (Ti _{1.89} Al _{0.22} Mn _{0.45} Fe _{0.13})] _{4.06.90}
	Murataite-5	(Ca _{1.30} La _{0.19} Zr _{0.76} Ti _{7.20} Al _{2.23} Mn _{2.17} Fe _{1.20}) _{15.0O_{24.76}}
	Murataite-8	(Ca _{0.76} La _{0.88} Zr _{0.42} Ti _{16.57} Al _{2.67} Mn _{2.60} Fe _{2.06}) _{26.0O_{45.81}}
	Perovskite	[(Ca _{0.72} La _{0.20})(Ti _{0.96} Al _{0.03} Mn _{0.01} Fe _{0.01})] _{1.92O_{3.0}}
	Crichtonite	[(Ca _{0.68} La _{0.81})(Zr _{0.33} Ti _{14.33} Al _{1.64} Mn _{2.12} Fe _{1.49})] _{21.39O_{38.0}}
Ce3	Zirconolite	[(Ca _{0.43} Ce _{0.07})Zr _{0.83} (Ti _{1.89} Al _{0.18} Mn _{0.46} Fe _{0.13})] _{4.0O_{6.93}}
	Murataite-5	(Ca _{1.74} Ce _{0.41} Zr _{1.67} Al _{1.22} Ti _{7.70} Mn _{1.75} Fe _{0.50}) _{15.0O_{25.42}}
	Murataite-8	(Ca _{2.27} Ce _{0.69} Zr _{1.01} Ti _{12.95} Al _{4.11} Mn _{3.17} Fe _{1.80}) _{26.0O_{43.27}}
	Perovskite	(Ca _{0.61} Ce _{0.24} Zr _{0.01} Ti _{0.95} Al _{0.05} Mn _{0.03}) _{1.89O_{3.0}}
	Crichtonite	(Ca _{0.84} Ce _{0.74} Zr _{0.24} Ti _{14.44} Al _{1.58} Mn _{2.07} Fe _{1.49}) _{21.41O_{38.0}}
Ce4	Murataite-5	(Ca _{1.62} Ce _{0.32} Zr _{1.51} Ti _{7.32} Al _{1.88} Mn _{1.76} Fe _{0.59}) _{15.0O_{25.21}}
	Murataite-8	(Ca _{0.88} Ce _{0.81} Zr _{0.41} Ti _{17.08} Al _{2.42} Mn _{2.37} Fe _{2.01}) _{26.0O_{46.15}}
	Perovskite 1	[(Ca _{0.69} Ce _{0.19})(Ti _{0.95} Al _{0.06} Mn _{0.03})] _{1.92O_{3.0}}
	Perovskite 2	[(Ca _{0.51} Ce _{0.32})(Ti _{0.99} Mn _{0.03} Fe _{0.01})] _{1.85O_{3.0}}
	Crichtonite	(Ca _{0.73} Ce _{0.67} Zr _{0.34} Ti _{14.06} Al _{2.0} Mn _{1.95} Fe _{1.66}) _{21.40O_{38.0}}
Nd	Zirconolite	[(Ca _{0.52} Nd _{0.16})Zr _{0.72} (Ti _{1.89} Al _{0.30} Mn _{0.32} Fe _{0.10})] _{4.0O_{6.88}}
	Murataite-5	(Ca _{2.21} Nd _{0.98} Zr _{3.12} Ti _{7.23} Al _{0.57} Mn _{0.70} Fe _{0.20}) _{15.0O_{26.20}}
	Murataite-8	(Ca _{2.88} Nd _{0.88} Zr _{1.74} Ti _{13.73} Al _{2.39} Mn _{3.08} Fe _{1.31}) _{26.0O_{43.76}}
	Perovskite	[(Ca _{0.58} Nd _{0.14})(Ti _{0.93} Al _{0.14} Mn _{0.07} Fe _{0.04})] _{1.91O_{3.0}}
	Crichtonite	(Mn _{2.91} Fe _{2.98} Ti _{14.28} Al _{1.43}) _{21.60O_{38.0}}
Ho	Zirconolite	[(Ca _{0.50} Ho _{0.48})Zr _{0.81} (Ti _{1.97} Mn _{0.20} Fe _{0.05})] _{4.0O_{7.04}}
	Murataite-5	(Ca _{3.10} Ho _{1.15} Zr _{1.98} Ti _{13.37} Al _{2.71} Mn _{2.72} Fe _{0.94}) _{26.0O_{43.76}}
	Murataite-8	(Ca _{1.33} Ho _{0.11} Zr _{0.23} Ti _{5.88} Al _{1.40} Mn _{1.17} Fe _{0.87}) _{11.0O_{18.31}}
	Perovskite	(Ca _{0.80} Ti _{1.0} Mn _{0.09} Fe _{0.03} Zr _{0.01} Ho _{0.04}) _{1.96O_{3.0}}
	Crichtonite	(Ca _{3.26} Ho _{0.19} Zr _{0.32} Ti _{12.85} Al _{2.34} Mn _{2.21} Fe _{1.55}) _{22.77O_{38.0}}

^a In the La, Ce4, Ho samples there is also pyrophanite-ilmenite of (Fe_{0.4}Mn_{0.6})TiO₃ composition and in the La sample in addition there are rutile.

Table 3. Electron binding energies (E_b^a , eV) and line widths (Γ^b , eV) of sample spectra

Sample	MO	Al 2p	Zr 3d _{5/2}	Ca 2p _{3/2}	Ti 2p _{3/2}	Mn 2p _{3/2}	Fe ²⁺ 2p _{3/2} , Fe ³⁺ 2p _{3/2}	Ln 3d _{5/2}	O 1s	C 1s
La	5.0, 7.0, 17.8, 20.6, 22.6, 25.5, 30.8, 37.6, 44.0, 48.6	74.3 (1.2)	182.6 (1.1)	347.4 (1.5)	458.9 (1.3)	641.4 (2.4), 4.6 sat ₁ (48%)	708.8 (1.7), 710.7 (3.0)	834.8 (2.1), 4.0 sat (82%)	530.3 (1.2), 531.9 (1.3)	285.0 (1.3), 289.0 (2.1)
Ce3	1.7, 4.9, 7.3, 18.1, 20.8, 22.6, 25.2, 30.8, 37.4, 43.7, 48.6	74.4 (1.4)	182.6 (1.3)	347.0 (1.5)	458.4 (1.4)	641.3 (2.5), 1.7 sat ₁ (21%), 5.8 sat ₂ (43%)	709.1 (1.7), 711.0 (3.0)	881.6 (3.2), 4.0 sat (133%)	530.2 (1.4), 531.6 (1.5)	285.0 (1.3), 289.1 (1.6)
Ce4	1.9, 4.9, 7.3 18.1, 20.9, 22.5, 25.2, 30.7, 37.4, 43.7, 48.7	74.3 (1.4)	182.6 (1.2)	347.0 (1.6)	458.8 (1.4)	641.5 (2.6), 4.3 sat ₁ (44%)	709.0 (1.7), 711.0 (3.0)	881.6 (2.9), 4.0 sat (173%)	530.2 (1.4), 531.6 (1.5)	285.0 (1.3), 288.9 (1.6)
Nd ^c	4.9, 7.4, 19.6, 22.4, 25.3, 30.7, 37.5, 43.8, 48.6, 50.8	74.2 (1.3)	182.6 (1.1)	347.1 (1.5)	458.8 (1.4)	641.4 (2.5), 4.6 sat ₁ (53%)	709.0 (1.7), 710.6 (3.0)	— 982.1 (5.0)	530.2 (1.3), 531.7 (1.4)	285.0 (1.3), 288.9 (1.8)
Ho ^d	4.5, 6.9, 10.3, 19.5, 22.1, 25.1, 30.6, 37.4, 43.5, 48.5, 50.9	74.1 (1.3)	182.6 (1.1)	346.9 (1.5)	458.7 (1.3)	641.4 (2.6), 5.4 sat ₁ (34%)	708.8 (1.7), 710.5 (3.0)	1352.5 (3.9)	530.2 (1.3), 531.7 (1.4)	285.0 (1.3), 288.9 (1.5)

^a E_b is given with respect to $E_b(\text{C } 1s) = 285.0$ eV;^b Γ are given in parentheses.^c Binding energies of Nd 4d-electrons are 122.5 (2.3) and 125.2 (2.9) eV.^d Binding energies of Ho 4d-electrons are 161.1(2.6), 163.4(1.8), 166.8(4.9) eV.

Core electron region. The elemental and ionic composition can be determined based on the intensities, energies, and structure of the core electron lines (Table 3): Mn 2p- (Fig. 4a), Fe 2p- (Fig. 4b), C 1s- (Fig. 4c), Zr 3d- (Fig. 4d), and Al 2p- (Fig. 5a), O 1s- (Fig. 5b), Ca 2p- (Fig. 5c), Ti 2p- (Fig. 5d) electrons. The structure of the spectrum of Mn 2p electrons (Fig. 4a) is typical of Mn³⁺ [29]. The spectrum of Fe 2p electrons of the samples has a complex structure (Fig. 4b); instead of a spin doublet with $\Delta E_{sl} = 13.1$ eV, a superposition of the spectra of Fe²⁺ and Fe³⁺ ions is observed [30]. There are components of this doublet for Fe²⁺ in the total spectrum as a shoulder on the complex structure of the Fe³⁺ spectrum in the region of lower binding energy at E_b (Fe 2p_{3/2}) = 709.1 eV with $\Gamma(\text{Fe } 2p_{3/2}) = 1.7$ eV (Fig. 4b). Fe³⁺ dominates in the samples; its amount is 92–94 rel %.

In the spectrum of C 1s electrons of carbon on the sample surface there is a line of the CO₃²⁻-group

(Fig. 4c). The spectrum of Zr 3d electrons consists of a doublet with $\Delta E_{sl}(\text{Zr } 3d) = 2.4$ eV (Table 3, Fig. 4d). The binding energy of Zr 3d_{5/2} electrons is close to the value for ZrO₂, equal to 182.6 eV [26].

The binding energy of Al 2p electrons for the studied ceramics is comparable to the value for Al₂O₃ [12] (Fig. 5a), for the Ca 2p_{3/2} electrons (Fig. 5c) it is approximately 346.0 eV, which is typical of CaO [25], and for the Ti 2p_{3/2} electrons (Fig. 5d) the binding energy depends little on the composition of the samples (Table 3). The spectrum of O 1s electrons consists of two lines (Fig. 5b, Table 3) at 530.2 and 531.6 eV with intensities of 85 and 15%, respectively. Taking into account Eq. (1) [25] the lengths of the element–oxygen R_{E–O} bonds are determined as 0.210 and 0.186 nm:

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

These values characterize the lengths of the element–oxygen bonds in the bulk of the studied samples and on their surfaces. It is assumed that the value of 0.210 nm is

Fig. 2. Survey spectra of ceramics using the example of (a) Ce4 and (b) La samples.

Fig. 3. Valence electron spectra of (a) Ce4, (b) La, (c) Nd, and (d) Ho ceramics.

Fig. 4. Spectra of (a) Al 2p-, (b) O 1s-, (c) Ca 2p-, and (d) Ti 2p-electrons of Ce4 ceramics.

averaged for the bond lengths of oxygen and metals (Al–O, Ca–O, Ti–O, Mn–O, Fe–O, Zr–O, Ln–O) present in the sample, and the value 0.186 nm refers to the bonds of metals with hydroxyl groups adsorbed on the surface from the environment.

The structure of the La 3d-electron spectrum of the La sample is due to spin-orbit splitting with $\Delta E_{sl} = 16.8$ eV [31] and many-body perturbation (Fig. 6a, Table 3) and is typical for the La^{3+} cation [14].

The structure of the spectra of Ce 3d electrons of the Ce3 and Ce4 samples is typical of a mixture of Ce^{3+} and Ce^{4+} ions (Figs. 6b, 6c). In [28], an original technique was proposed, which makes it possible to determine the ionic composition of the sample surface (the ratio of the Ce^{3+} and Ce^{4+}) based on the intensity of a single line of the spectrum of Ce 3d electrons at 916.8 eV. It was found that the Ce4 sample contains 25 rel % Ce^{4+} and 75 rel % Ce^{3+} , and Ce3 contains, 26 rel % Ce^{4+} and 74 rel % Ce^{3+} . The Ce^{3+} state dominates regardless of the form in which the element (CeO_2 or Ce_2O_3) was introduced into the charge. This fact agrees with the

X-ray absorption spectroscopy (XAS) data, according to which cerium in these samples there is predominantly in the Ce^{3+} state [23].

The complex structure of the spectrum of Nd 3d electrons for the Nd sample, caused by spin-orbit splitting with $\Delta E_{sl} = 22.2$ eV [14], multiplet splitting, and multielectron excitation, is superimposed on the structure of the O KLL Auger spectrum of oxygen (Fig. 7c). Despite this fact, it was possible to determine the binding energies of electrons of the spin doublet lines, equal to $E_b(\text{Nd } 3d_{5/2}) = 982.1$ eV and $E_b(\text{Nd } 3d_{3/2}) = 1005.2$ eV, which are characteristic of Nd^{3+} in Nd_2O_3 [14] (Fig. 7c, Table 3). The spectrum of Nd 4d electrons with $\Delta E_{sl} = 9.9$ eV [32] is superimposed on the spectrum of aluminum Al 2s (Fig. 7a). However, the observed two maxima at 122.5 and 125.2 eV are characteristic of the Nd 4d electrons of the Nd^{3+} cation in Nd_2O_3 [14].

The spectrum of Ho 3d_{5/2} electrons of the Ho sample with $\Delta E_{sl} = 40.1$ eV [31] is observed at a weighted average binding energy of 1351.2 eV (Fig. 7d). There is a maximum at 1352.5 eV, which corresponds to the bind-

Fig. 5. Spectra of (a) Al2p, (b) O1s, (c) Ca2p- and (d) Ca2p-electrons of Ce4 ceramics.

Fig. 6. REE spectra of 3d electrons (La or Ce) for (a) La, (b) Ce3, and (c) Ce4 ceramics.

Fig. 7. Spectra of (a) Nd 4d and (b) Ho 4d electrons, and (c) Nd 3d and (d) Ho 3d electrons for ceramics with neodymium (Nd sample) and holmium (Ho sample).

ing energy of Ho 3d_{5/2} electrons in Ho₂O₃. The observed maxima in the spectrum agree with the data for Ho³⁺ in Ho₂O₃ [14]. The structure of the spectrum of Ho 4d electrons of the Ho sample with $\Delta E_{sl} = 11.3$ eV [32] partially overlaps with the spectrum of 3d electrons of Zr (Fig. 7b). Therefore, the intensity of the spectral lines of 4d electrons and the holmium content are determined with a large error. When detecting the oxidation state of metals in the studied ceramics samples, the data of [33] were used.

The XPS method allows the analysis of the composition and valence state of elements on the sample surface to a depth of 10 nm [27]. This makes it indispensable in the analysis of changes in matrices after interaction with a solution [34]. The question remains to what extent the data for this layer can be extended to bulk of the ceramics. There is some discrepancy between the XPS

and XAS results of the samples, manifested in a smaller share of oxidized forms of Ce and U when analyzed by the XAS method [22, 23]. This fact may be due to the oxidation of elements on the sample surface during storage in air. When studying brannerite, it was shown that the share of such uranium is estimated at 10% of its total amount [35]. To reduce the influence of this factor, a fresh cleavage of the bulk sample was made before the XPS study. Another reason for the differences between the XPS and XAS data is a more rough estimate of the ratio of oxidation states by the XAS method. Therefore, XPS gives a more correct estimate of the contents of cations of different valences. The study of Ce-brannerite showed [36] that the discrepancy between the XPS data for the sample surface and the XAS data for the volume is relatively small. Note that data on the composition and valence of elements in the surface layer is very im-

Table 4. Elemental composition of the surface of the studied samples according to XPS data and their target bulk composition normalized to one zirconium atom^a

Sample	Data type	Elemental composition per 1 Zr atom
La	XRS, surface	Al _{1.24} Ca _{1.79} Ti _{6.47} Mn _{2.32} Fe _{1.10} Zr _{1.00} La _{1.17} O _{22.65+3.22} C _{5.13+1.02}
	Bulk composition	Al _{1.22} Ca _{2.20} Ti _{7.75} Mn _{1.43} Fe _{0.77} Zr _{1.00} La _{0.75} O _{26.7}
Ce3	XRS, surface	Al _{1.27} Ca _{1.72} Ti _{6.62} Mn _{2.57} Fe _{1.41} Zr _{1.00} Ce _{0.92} O _{22.23+5.22} C _{8.53+0.96}
	Bulk composition	Al _{1.22} Ca _{2.20} Ti _{7.76} Mn _{1.43} Fe _{0.78} Zr _{1.00} Ce _{0.70} O _{29.80}
Ce4	XRS, surface	Al _{1.28} Ca _{1.78} Ti _{6.36} Mn _{2.18} Fe _{1.27} Zr _{1.00} Ce _{0.64} O _{20.87+3.93} C _{6.50+1.00}
	Bulk composition	Al _{1.23} Ca _{2.21} Ti _{7.77} Mn _{1.43} Fe _{0.78} Zr _{1.00} Ce _{0.72} O _{27.07}
Nd	XRS, surface	Al _{1.27} Ca _{1.77} Ti _{6.74} Mn _{2.47} Fe _{0.93} Zr _{1.00} Nd _{0.80} O _{22.49+3.32} C _{6.46+0.93}
	Bulk composition	Al _{1.23} Ca _{2.20} Ti _{7.76} Mn _{1.43} Fe _{0.77} Zr _{1.00} Nd _{0.74} O _{26.71}
Ho	XRS, surface	Al _{1.20} Ca _{1.70} Ti _{6.55} Mn _{1.83} Fe _{0.99} Zr _{1.00} Ho _{0.70} O _{23.18+3.47} C _{5.37+0.79}
	Bulk composition	Al _{1.22} Ca _{2.21} Ti _{7.77} Mn _{1.43} Fe _{0.77} Zr _{1.00} Ho _{0.65} O _{26.60}

^a The composition is given for two chemical states for oxygen and carbon (Figs. 4, 5).

portant, since this region of the matrix is exposed to the solution. Leaching from matrices of variable valence elements (III, IV) is higher in cations of lower charge and higher basicity, i.e., in Ce³⁺ and Pu³⁺, and their ability to form complexes is lower than that of Ce⁴⁺ and Pu⁴⁺ [37, 38]. According to XPS data, the surface composition of the samples (Table 4) is somewhat different from the bulk composition of ceramics (Table 1). Further sample studies are required to understand the exact reasons for this discrepancy.

CONCLUSIONS

Samples of a potential matrix for the immobilization of actinides and lanthanides, consisting mainly of murataite, zirconolite, and perovskite, have been studied. The XPS method was employed to determine the composition and valence state of elements in the surface layer of samples up to 10 nm thick. The content of Mn and Fe therein is higher, that of Ca and Ti is lower than in the bulk compositions in the samples. The ratio of Ce³⁺ and Ce⁴⁺ in the samples is 3 : 1 regardless of the form of cerium introduction into the charge. Iron is in the form of Fe³⁺ (92–94 rel %) and Fe²⁺ (6–8 rel %), and manganese is present in the Mn³⁺ state. The average bond length of Al–O, Ca–O, Ti–O, Mn–O, Fe–O, Zr–O, Ln–O was estimated as 0.210 nm.

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CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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