XPS study of ion irradiated and unirradiated CeO$_2$ bulk and thin film samples

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**Abstract**

This work considers the effect of fission-energy ion irradiation on the electronic structure at the surface of bulk and thin film samples of CeO$_2$ as a simulant for UO$_2$ nuclear fuel. For this purpose, thin films of CeO$_2$ grown on Si substrates and bulk CeO$_2$ samples were irradiated by Xe ions (92 MeV, $4.8 \times 10^{15}$ ions/cm$^2$) to simulate the fission damage that occurs within nuclear fuels. The irradiated and unirradiated samples were characterized by X-ray photoelectron spectroscopy. A technique of the quantitative evaluation of cerium ionic composition on the surface of the samples has been successfully applied to the obtained XPS spectra. This technique is based on the intensity of only one of the reliably identifiable high-energy peak at 916.6 eV in the Ce 3d XPS spectra. The as-produced samples were found to contain mostly Ce$^{4+}$ ions with a small fraction of Ce$^{3+}$ ions formed on the surface in the air or under X-rays. The core-electron XPS structure of CeO$_2$ was associated with the complex final state with vacancies (holes) resulting from the photoemission of an inner electron. The Xe ion irradiation was found to increase the Ce$^{3+}$ content in the samples of CeO$_2$, with the thin films being more sensitive than the bulk samples.

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1. Introduction

Cerium dioxide, CeO$_2$, is a fluorite structure ceramic widely used as an inactive structural surrogate to UO$_2$ and PuO$_2$ to avoid difficulties associated when working with radioactive materials [1,2]. This material is suggested to be used as an inert matrix for perspective nuclear fuels and highly radioactive waste disposal [1,3]. Irradiation studies, where CeO$_2$ is exposed to ions with different mass and energy, are extensively taking place in the recent time [1,2,4–12]. The attempt of these studies is to replicate the effect of radiation damage by fission fragments that is taking place within nuclear fuels. The irradiated and unirradiated samples were characterized by X-ray photoelectron spectroscopy (XPS) proved to be an effective tool for determination of the cerium ionic composition (Ce$^{3+}$ and Ce$^{4+}$).

Unfortunately, the available literature does not reveal any information on dissolution mechanism of CeO$_2$ in water, but it is widely accepted that CeO$_2$ dissolves via reduction of Ce$^{4+}$ to Ce$^{3+}$ under air atmosphere [19]. It is also known that fission-energy ion irradiations of CeO$_2$ cause a partial reduction of Ce$^{4+}$ to Ce$^{3+}$ [7,20,21], which enhances its dissolution [19]. As a result, there is a practical need in a technique for quantitative evaluation of cerium ionic composition on the surface of CeO$_2$ samples to inform on their aqueous durability.

XPS determination of the cerium oxidation state in compounds faces difficulties due to the complex structure in the valence- and core-electron spectra [22–31]. Thus, the Ce 3d XPS spectra of the Ce$^{3+}$ ions beside the primary peaks show sometimes the satellites with a higher intensity compared to the primary peaks [27,28,32–36]. The Ce 3d XPS spectra of CeO$_2$ show even more complicated structure [7,23,27,31,33–38] as compared to the spectra structure of Ln$_2$O$_3$ [22,23]. The majority of the available literature suggests that CeO$_2$ contains a mixture of Ce$^{3+}$ and Ce$^{4+}$ ions (mixed valence) [24–26,39,40]. However, the authors of Ref. [41] showed on the basis of the calculations that CeO$_2$ contain only Ce$^{4+}$ ions, and the Ce 3d structure appears due to the complex final state containing the ground state Ce 3d$^9$4f$^0$ and two exited final states 3d$^9$4f$^0$OVMO$^{-1}$ and 3d$^9$5p$^n$p$^1$. These results agree with the experimental data of Ref. [42]. An unusual final state Ce 3d$^9$5p$^n$p$^1$ can be associated with the screened vacancy in the inner valence molecular orbitals (IVMO) [23,43]. The formation of such a vacancy agrees with the unusually high (16 eV) binding

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energy (BE) shift of the peaks associated with the final state Ce 3d^{5}p^{5}n^{1} relative to the peaks associated with the ground final state Ce 3d^{5}4f^{6}.

The complex XPS structure parameters can be used for qualitative identification of physicochemical properties in various cerium compounds [23] and the main attention is focused on the Ce 3d structure. Thus, on the basis of many Ce 3d XPS parameters, the authors of Ref. [44] suggest a technique of quantitative determination of the cerium ionic composition (Ce^{3+} and Ce^{4+}) in different compounds. The authors of Refs. [7] and [20] determined the Ce^{3+} concentration after irradiation of CeO2 with 200 MeV Xe ions by direct subtraction of the Ce 3d spectrum of the Ce^{6+} ions of a standard sample from the Ce 3d spectrum of the irradiated sample. Similar techniques were used in Refs. [32,33,45–47].

This work considers the explicit effect of radiation damage by fission-energy ions on non-stoichiometry in CeO2 as an inactive analogue to the UO2 matrix of nuclear fuel and outlines a methodology developed for determining the degree of non-stoichiometry in CeO2-x. For this purpose, thin films of CeO2 on Si substrates and bulk CeO2 samples were irradiated with \(^{129}\)Xe\(^{2+}\) ions of 92 MeV to a fluence of \(4.8 \times 10^{15}\) ions/cm\(^2\) to simulate the damage produced by fission fragments in nuclear fuel. The irradiated and unirradiated samples were analyzed using a quantitative analysis technique of the XPS spectra described in Ref. [35] and the obtained results were compared.

The XPS spectra in the present work were taken from the surface of single-crystal CeO2 film in the BE range of 0–1250 eV in order to illustrate the complex structure formation in the Ce 3p\(\gamma\), 3d-, 4s-, 4p-, 4d-, 5s- spectra (and the absence of the complex structure in the Ce 5p spectrum, where the quasi-core hole appears). Each of the measured spectra allowed a quantitative ionic composition to be evaluated on the basis of the technique considered in Ref. [35]. For the bulk samples the XPS spectra were measured for certain shells. A similar work has been done using UO2 thin films in Ref. [48].

### 2. Experimental section

#### 2.1. Sample production and irradiation

The CeO2 thin films were grown by pulsed laser deposition (PLD) on three (001) oriented p-doped Si substrates and characterized as described in detail in Ref. [19]. The thin films of CeO2 were nominally of the same thickness (250 nm), as they were deposited by the same number of laser pulses, the three samples produced had different colors. This is an indication that the thin films may have had different thicknesses [49]. X-ray diffraction (XRD) analysis suggested that the CeO2 films of samples AP1 and AP3 can be described as single crystals in (1 1 1) crystallographic orientation and the CeO2 film of sample AP2 is preferentially oriented in (1 1 1) with (0 0 1) domains also present. Sample AP1 was left as a benchmark for comparison and samples AP2 and AP3 were irradiated with Xe ions. The bulk samples of CeO2 were obtained from Sigma-Aldrich in the form of fused pieces 3–6 mm in size and 99.9% purity on trace metal basis, as claimed by the supplier. Table 1 summarizes the produced and irradiated samples.

| Sample name | Sample description |
|-------------|--------------------|
| AP1         | Unirradiated thin film sample |
| AP2g        | \(^{129}\)Xe\(^{2+}\) irradiated thin film sample |
| AP3g        | \(^{129}\)Xe\(^{2+}\) irradiated thin film sample |
| AP4         | Unirradiated bulk sample |
| AP4g        | \(^{129}\)Xe\(^{2+}\) irradiated bulk sample |
| APS         | Unirradiated bulk sample |
| AP5g        | \(^{129}\)Xe\(^{2+}\) irradiated bulk sample |

| Binding energy (eV) |
|---------------------|
| Intensity (arb. units) |

**Fig. 1.** XPS survey-scan of CeO2 film (sample AP1).

These samples were studied earlier by XRD and scanning electron microscopy (SEM) and dissolution experiments were also performed to assess the effect of induced radiation damage on aqueous durability of the CeO2 matrix in Ref. [19].

To simulate the damage produced by fission fragments in nuclear fuel, the samples were irradiated with 92 MeV energy \(^{129}\)Xe\(^{2+}\) ions to a fluence of \(4.8 \times 10^{15}\) ions/cm\(^2\) on the IRRSUD beamline at the GANIL accelerator, Caen, France, with a detailed description given in Ref. [19]. The SRIM code [50] indicated that the projected ion range in CeO2 is \(\sim 7.5\) μm and Xe ions completely penetrate the CeO2 thin films (250 nm max) and stop in the substrate at a depth of \(\sim 13.5\) μm beneath the sample’s surface. The electronic stopping regime dominates the dissipation of ion energy throughout the entire film [19].

#### 2.2. X-ray photoelectron measurements

X-ray photoelectron spectra of the CeO2-x samples were recorded on a Kratos Axis Ultra DLD spectrometer using monochromatic Al-Kα radiation (\(hv = 1486.7\) eV) at 150 W X-ray gun power under 1.3 \(\times 10^{-7}\) Pa at room temperature (Fig. 1). The analyzed area was an ellipse with 300 and 700 μm minor and major axes, respectively. Binding energy scale of the spectrometer was preliminarily calibrated by the position of the peaks of Au 4f\(7/2\) (83.96 eV) and Cu 2p\(3/2\) (932.62 eV) core levels for pure gold and copper metals. The spectra were acquired in the constant analyzer energy mode using the pass energy of 20 eV and a step size of 0.05 eV.

All the spectra were recorded as a sequence of one scan acquisition for each spectrum starting with the higher BE ones. The sequence was cycled until a certain spectrum measurement had reached a required number of scans, then the measurement of this spectrum would stop. The number of scans for each spectral peak was different depending on the intensity of this peak in the survey spectrum. This provided reliable spectral data and a correct BE calibration relative to the E\(_{\text{g}}\)(C 1s), peak width calibration relative to the I(C 1s), as well as the intensity calibration relative to the standard peak (e.g., Ce 3d).

The Kratos charge neutraliser system was used and BEs were measured relative to the BE of the C 1s electrons from hydrocarbons adsorbed on the sample surface that was accepted to be equal to 285.0 eV on the gold plate E\(_{\text{g}}\)(Au 4f\(7/2\)) = 84.0 eV and E\(_{\text{g}}\)(C 1s) =...
284.1 eV. These values have to be taken into account for comparison of the present data with the data of other authors. The equipment resolution measured as the full width at half maximum (FWHM) of the Au 4f7/2 peak was less than 0.65 eV. The FWHMs are given relatively to that of the C 1s XPS peak from hydrocarbon on the sample surface being 1.3 eV [51]. The error in the determination of the BE and the peak width did not exceed ±0.05 eV, and the error of the relative peak intensity – ±5%. The inelastically scattered electron-related background was subtracted by the Shirley method [52].

A quantitative elemental analysis was performed for the surface of the studied samples. It was based on the fact that the spectral intensity is proportional to the number of certain atoms in the studied samples. It was based on the fact that the spectral intensity is proportional to the number of certain atoms in the XPS spectrum, using the calibration coefficient and the relative core–shell spectral intensity, $I_0$ is the relative core–shell spectral intensity, $I/k$ is the relative experimental sensitivity coefficient. The following coefficients relative to the C 1s were used: 1.00 (C 1s); 2.81 (O 1s); 0.119 (O 2s); 31.68 (Ce 3d); 0.68 (Ce 4s); 3.83 (Ce 4p); 8.860 (Ce 4d).

### 2.3. Determination of the ionic composition in CeO$_{2-x}$ oxides

On the basis of the Ce 3d XPS structure and the technique described in Ref. [35] cerium ionic composition (Ce$^{3+}$ and Ce$^{4+}$) of the studied samples was evaluated. The point of this technique was the following. The Ce 3d XPS of the Ce$^{4+}$ ion consists of six peaks (1–6) corresponding to different final states after the Ce 3d electron photoemission (for line identification of this structure see Section 3, Fig. 2a). The Ce 3d XPS spectrum of a Ce$^{3+}$ ion consists of four peaks located near the peaks (1, 4) and (2, 5) of the Ce$^{4+}$ XPS spectrum (Fig. 2b, Ref. [35]). In the case of Ce$^{3+}$ and Ce$^{4+}$ mixture, the XPS spectrum is complicated. The feature $I_0(6)$ at 916.4–916.6 eV remains well pronounced (Fig. 2b). Shake-up satellites (3, 6) (Fig. 2a) are the Ce 3d spin-orbit doublet with $\Delta E_{4d}$(Ce 3d) = 18.3 eV and shifted by 16.0 eV to the higher BE side relative to the spin-orbit doublet (1, 4) of the ground state. This doublet allows the most precise determination of the Ce 3d spin-orbit splitting. Since the feature (3) is the low-BE component of the spin-orbit doublet (3, 6), its intensity is (3/2) of $I_0$. Features (1, 2, 3) characterize only the Ce 3d$_{5/2}$ spectrum. For the standard CeO$_2$ sample the intensity ratio (1, 2) to (3) is $a_0 = I_0(3)/(3/2)I_0(6)$, where $I_0$ is the intensity of features (1, 2), $I_0(6)$ is the intensity of feature (6) of standard Ce$^{4+}$ spectrum, and $a_0$ is a calibration coefficient. Since the Ce 3d$_{3/2}$ XPS features of the Ce$^{3+}$ ions for the Ce$^{3+}$ and Ce$^{4+}$ mixture lies in the BE range of the features (1, 2) of Ce$^{4+}$ XPS spectrum, using the calibration coefficient $a_0$ one can find the Ce$^{3+}$ contribution to the XPS intensity. If for the XPS spectrum of the Ce$^{3+}$ and Ce$^{4+}$ mixture $I_0$ is the intensity of feature (6); (3/2)$I_0$ is the intensity of feature (3); $a_0$ is the calibration coefficient; $I$ is the intensity of features (1–2), including the Ce 3d$_{3/2}$ intensity from the Ce$^{4+}$ ions, then $a_0(I_0/3)$ is the contribution of the intensity of the Ce$^{4+}$ ions to $I$; and $I – a_0(I_0/3)$ is the contribution of the Ce$^{3+}$ in the intensity $I$. Since the total Ce 3d$_{3/2}$ intensity of the peaks (1–2–3) from the Ce$^{3+}$ and Ce$^{4+}$ ions is $I + (3/2)I_0$, the fraction $v_1$($\text{Ce}^{3+}$) of the Ce$^{3+}$ ions can be found as the ratio $[I – a_0(I_0/3)]/[I + (3/2)I_0]$:

$$v_1(\text{Ce}^{3+}) = \frac{[I – a_0(3/2)I_0/I]}{[I + (3/2)I_0/I]} \quad (1)$$

and the fraction $v_2$($\text{Ce}^{4+}$) $v_2(\text{Ce}^{4+}) = 1 – v_1(\text{Ce}^{3+})$. $v_2(\text{Ce}^{4+})$ is the intensity of feature (6) relative to the spin-orbit doublet (1, 4) of the ground state.

As shown in the current work (Section 3), the similar expressions can be drawn using the Ce 3p$_{3/2}$, 4s, 4p, 4d, 5s XPS structure parameters as well (Figs. 3–7). The results of Eqs. (1) and (2) for the surfaces of K-Ke-Ti ceramics are in a good agreement with the XRD and SEM-EDS data characterizing the bulk of the samples in Ref. [35].

### 3. Results and discussion

The obtained results were discussed in the approximation that the standard CeO$_2$ sample contains only Ce$^{4+}$ ions [42]. The survey XPS scans of all the studied cerium dioxide samples (Table 1) except for AP3g showed the XPS and Auger features only from cerium, oxygen and carbon (Fig. 1). The survey scan of AP3g showed extra peaks from Si 2s and 2p due to the film fragmentation under the Xe irradiation, which was seen in SEM (see Fig. 4 in Ref. [19]). Silicon was not observed in the XPS scans of AP1 and AP2g since their thickness (~250 nm) exceeded the photoelectron escape depth (~5 nm). The survey XPS scans are in satisfactory agreement with the data in Refs. [53] and [54].

#### 3.1. The structure of XPS spectra of valence electrons

The valence (from 0 to ~50 eV BE) XPS structure of sample AP1 (Fig. 3a) differs slightly from the corresponding structure of CeO$_2$...
Fig. 3. Valence XPS narrow-scans of the CeO$_2$ thin film samples: (a) unirradiated CeO$_2$ surface (sample AP1); (b) $^{129}$Xe$^{23+}$ irradiated surface (sample AP3g). Numbers (1, 2) denote the final states (see Fig. 2). Peak (3) at 51.7 eV is not shown.

Fig. 4. Ce 4d XPS narrow-scan of unirradiated CeO$_2$ surface (sample AP1). Numbers (1–6) denote the final states (see Fig. 2).

Fig. 5. Ce 4p XPS narrow-scan of unirradiated CeO$_2$ surface (sample AP1). Numbers (1–5) denote the final states (see Fig. 2). Peak (6) at 237.1 eV is not shown.

Fig. 6. Ce 3p$_{3/2}$ XPS narrow-scan of unirradiated CeO$_2$ surface (sample AP1). Numbers (1, 2, 3) denote the final states (see Fig. 2). Peaks (4, 5, 6) at 1270.2, 1276.5 and 1285.9 eV are not shown.

Fig. 7. XPS narrow-scans of Ce 4s and C 1s of unirradiated CeO$_2$ surface (sample AP1). Numbers (1, 2, 3) denote the final states (see Fig. 2).
samples in Refs. [23] and [42]. Beside the structures associated with the outer (OVMO) and inner (IVMO) valence molecular orbitals, this spectrum shows a low-intensity peak at 1.1 eV associated with the unbound Ce 4f electrons (Table 2) of the Ce³⁺ ions formed on the surface in the air and/or under the X-ray beam in the spectrometer chamber [34,44,55,56]. The Ce 4f peak must be absent for compounds containing only Ce⁴⁺ ions, while for compounds containing Ce³⁺ ions this peak must have a high intensity being an important characteristic of the Ce³⁺ ions [23,42]. This was confirmed by the absence of the Ce 4f peak in the photoelectron spectrum (350 eV excitation) of a single-crystalline CeO₂(1 1 0) film on a SrTiO₃(2 1 1) single crystal substrate in Ref. [57], in the spectrum of valence electrons of a CeO₂ film on a Ge substrate [58] and in the valence electron resonant emission spectrum (Ce 4f → Ce 4d¹) of cerium dioxide samples in Ref. [57]. The Ce 4f peak is also absent in the spectrum of a fresh CeO₂ powder pressed in an indium holder measured under the AlKα X-ray beam exposure for ~20 min in Ref. [42]. The resonant emission spectrum of CeO₂, as expected, shows the intense Ce 4f peak at 1.9 eV [57]. The authors of Ref. [57] showed that Ce⁴⁺ ions on the surface of CeO₂ powder samples reduce to Ce³⁺ ions under the X-ray irradiation faster than on the surface of sintered samples. Such partial Ce⁴⁺ to Ce³⁺ reduction also takes place during heating of a CeO₂ sample up to 900 °C in a sample chamber of the XPS spectrometer [59,60]. The examined samples can also be heated under the AlKα X-ray irradiation. Therefore, the low-intensity peak at 1.1 eV in the XPS spectrum of sample AP1 (Fig. 3a) should be attributed to Ce³⁺ ions formed under the excitation X-ray beam. Since the Ce³⁺ ion content in sample AP1 is just several percent, the main XPS structure typical for Ce⁴⁺ ions remains.

The intensity of the peak associated with the unbound Ce 4f electrons $I_{Ce4f} = \frac{I(Ce4f)}{I(Ce5s)}$ relative to the intensity of the Ce 5s peak taking into account the satellite intensities and with the photoionization cross-sections in mind [61,62] allowed a quantitative evaluation of the number of the Ce 4f electrons per one cerium atom $n_{Ce4f}$ for the studied samples (Table 3) with the accuracy of ±5%, since the Ce 4f intensity is very low compared to the Ce 5s intensity. These data show that for sample AP1 $n_{Ce4f} = 0.03$ and this sample contains 3% of Ce⁴⁺ ions. An XPS spectrum of sample AP1 contains mostly the Ce⁴⁺-related structure with weak Ce³⁺-related features.

The OVMO spectrum of sample AP1 show two peaks at 3.9 and 5.8 eV and is 3.4 eV wide ($I(GVMO) = 3.4$ eV) (Fig. 3a, Table 2). On the basis of the valence resonant emission spectral structure of CeO₂ [57] and non-relativistic calculation results for the CeO₂₁²³ cluster [43] the peak at 3.9 eV can be attributed to the Ce 4f – O 2p states, and the peak at 5.8 eV – to the Ce 5d – O 2p states. The XPS spectra of cerium dioxide films contain mostly the Ce⁴⁺-related structure with weak Ce³⁺-related features.

### 3.2. The structure of XPS spectra of inner electrons

The Ce 5s XPS structure contains the primary line at $E_p(Ce5s) =$ 36.7 eV with a width $I'$(Ce 5s) = 2.3 eV and at 6.9 eV away from the primary peak exhibits a 4% intensity satellite associated with the charge transfer effect during the photoemission, and a ~50% intensity shake-up satellite 15 eV away from the primary peak, which is not shown in Fig. 3a but indicated in the survey spectrum (Fig. 1) with an arrow. It should be noted, that such satellites are absent

### Table 2

Electron binding energies $E_b$(eV), FWHM $\Gamma$(eV), satellite positions $E_{sat}$(eV) of the unirradiated (AP1, AP4, AP5) and ¹²⁹Xe²⁺ irradiated (AP2g, AP3g, AP4g, AP5g) cerium dioxide films and bulk samples.

| Sample | Ce 4f | OVMO | Ce 5p₂/₃ | Ce 5s | Ce 4d₂/₃ | Ce 4p₂/₃ | Ce 4s | Ce 3d₂/₃ | O 1s |
|--------|-------|------|---------|-------|---------|---------|------|---------|-----|
| AP1    | 1.1   | 3.9  | 17.3    | 36.7  | 6.9 sat1 | 108.2  | 6.6 sat1 | 882.1  | 529.4 |
|        |       | 5.8  |         |       |         | (2.7)   |       | (1.8)   | (1.0) |
| AP2g   | 1.1   | 4.0  | 17.6    | 36.9  | 6.8 sat1 | 206.5  | 13.7 sat1 | 531.3  | 288.9 |
|        |       | 5.9  |         |       |         |         |       | (2.1)   | (2.0) |
| AP3g   | 1.9   | 4.1  | 18.2    | 36.7  | 6.8 sat1 | 289.9  | 13.7 sat1 | 531.1  | 271.3 |
|        |       | 5.7  |         |       |         |         |       | (1.7)   | (1.8) |
| AP4    | 1.2   | 3.9  | 17.7    | 36.7  | 6.7 sat1 | 288.8  | 16.2 sat1 | 531.8  | 16.0 |
| AP4g   | 1.3   | 4.1  | 18.0    | 36.8  | 6.8 sat1 | 289.0  | 16.0 sat1 | 532.2  | 14.9 |
| AP5    | 1.2   | 3.8  | 17.2    | 36.8  | 6.7 sat1 | 289.0  | 15.9 sat1 | 532.2  | 14.9 |
| AP5g   | 1.3   | 3.7  | 17.4    | 36.8  | 6.8 sat1 | 289.9  | 15.8 sat1 | 532.2  | 14.9 |
| CeO₂   | 1.4   | 5.8  | 17.8    | 36.8  | 6.8 sat1 | 288.8  | 15.7 sat1 | 530.0  | 162.0 |
| CeNbO₄ | 1.6   | 5.8  | 17.8    | 36.8  | 6.8 sat1 | 288.8  | 15.7 sat1 | 530.0  | 162.0 |

a BEs are given relative to the $E_b$(C 1s) = 285.0 eV.

b FWHMs $\Gamma$(eV) are given in the parenthesis.

c Satellites $s_2$ are associated with the charge transfer effect, $s_1$ – with the shake-up process.

d Ce 3p₂/₃ spectrum consists of two peaks at 1183.2(7.4) and 1198.9(3.9) eV.

e BEs are given relative to the $E_b$(C 1s) = 285.0 eV for powders of CeO₂ and CeNbO₄ [42].
in the Ce 5p spectrum. On the one hand, the absence of intense satellites in the Ce 5p spectrum agrees with the fact that the Ce 5p electrons are not atomic and participate in the chemical bond formation. On the other hand, this experimentally corroborates that the Ce 5p electrons participate in the shake-up process responsible for the intense satellites at the higher BE side from the primary peaks (sat 2) in the core-electron XPS spectra of CeO 2 (Figs. 2, 4–6 in Refs. [36,42]).

The Ce 3d XPS structure of sample AP1 instead of the expected spin–orbit split (ΔEg(Ce 3d) = 18.6 eV) of two peaks exhibits a complex structure due to a complex final state after the Ce 3d electron photoemission (Fig. 2a, Table 2, Refs. [37,42]). One can separate six principal features in this structure (1–6) (Fig. 2a). The final state consists of three separate final states with holes: Ce 3d 5p 0 – ground final state (1, 4) results in the spin-doubled (ΔEg(Ce 3d) = 18.6 eV) in the spectrum; Ce 3d 4 f 0 4p 0 5p 0 (3) (Fig. 6). The state Ce 3d 5p 0 4p 0 5p 1 4f 1 VMO 1 – charge transfer related satellites (2, 5) and Ce 3d 5p 0 4p 0 5p 1 – shake-up satellites (3, 6) with ΔEg(Ce 3d) = 16.0 (15.7) eV (Refs. [41,42], Fig. 2a). The state Ce 3d 5p 0 4p 0 5p 1 unlike the other states contains an extra quasi-core hole Ce 5p 1 resulting in a strong shift of the doublet (3, 6) toward the higher BE side relative to the doublet (1, 4), which is associated with the ground final state. The total intensity of all the complex structure for the standard stoichiometric CeO 2 corresponds to Ce 3d electrons of the Ce 4+ ions only [35,42,63]. In Ref. [41] it is mentioned that the Ce 3d 4f 0 4p 0 VMO 1 state involves a 4f-electron. This results in multiplet splitting of the duplet. In other words, it is possible to say that the duplet lines of the Ce 3d 4f 0 4p 0 (1, 4) and Ce 3d 5p 0 4p 1 5p 1 (3, 6) states must be narrow and the duplet lines of the Ce 3d 4f 0 4p 0 VMO 1 (2, 5) state will have a complex shape (see Fig. 2a). This shape is difficult for accounting during decomposition of the spectrum into components.

The complex structure in the Ce 4d XPS of sample AP1 (Fig. 4) also consists of 6 features and, as in the case of the Ce 3d XPS structure corresponds to the complex final state of cerium ions [42]: Ce 4d 5f 0 – ground final state (1, 4) resulting in the spin-doubled (ΔEg(Ce 4d) = 3.2 eV); Ce 4d 4f 0 4p 0 VMO 1 – charge transfer related satellites sat (2, 5) with ΔEg(Ce 4d) = 6.6 eV; and Ce 4d 5p 0 4p 0 5p 1 – shake-up satellites (3, 6) with ΔEg(Ce 4d) = 13.7 eV (Fig. 4, Table 2). At 104.4 eV BE one can see a very weak feature corresponding to Ce 5+ ions present [55], which agrees with the weak feature in the valence band of the Ce 4f XPS spectrum (Fig. 3a).

The Ce 4p XPS structure is even more complicated compared to the Ce 4d one due to the fact that the Ce 4p spectrum exhibits the dynamic effect related structure (like the Ba 4p and La 4p XPS structure in compounds considered in Refs. [64,85]) together with the structures related to the spin-orbit splitting and the satellites. The dynamic effect appears due to the extra two-hole final state Ce 4p 0 4d 0 5p 0 4f 1 VMO 1, which results in the smearing of the primary structure, especially the Ce 4p 1/2 component (Fig. 5). Five unmarked extra peaks in Fig. 5 are attributed to the dynamic effect. Despite this, one can see six components (1–6) quantitatively characterizing the Ce 4+ ion. Ce 4p 1/2 VMO 1 – charge ground final state (1, 4); Ce 4p 3/2 VMO 1 – charge ground final state (2, 5) and Ce 4p 5/2 VMO 1 – shake-up satellites (3, 6). Feature (6) is observed at the higher BE side from the (3) at 17 eV is not shown in Fig. 5. The Ce 3p 1/2 spectrum, as well as the Ce 4p 1/2 one, exhibits three features (1–3) associated with the final states: Ce 3p 1/2 VMO 1 (1); Ce 3p 3/2 VMO 1 (2) and Ce 3p 5/2 VMO 1 (3) (Fig. 6).

The spectrum of Ce 4s electrons is observed toward high energies of bonding from the Ce 1s peak of saturated hydrocarbons with the intensity Ic 1s (C 1s/Ce 3d) = 1.44 is observed at 285.0 eV (Fig. 7). The Ce 4s spectrum, like the Ce 3s one (Fig. 3a), consists of three features (1–3), corresponding to the final states: Ce 4s 1/2 – ground final state (1); Ce 4s 3/2 VMO 1 – 4% intensity charge transfer related satellite (2); and Ce 4s 5/2 VMO 1 – 50% intensity shake-up satellite. The observed complex structure in the XPS spectrum of the film in sample AP1 corresponds mostly to that of bulk samples AP4, AP5 and CeO 2 samples in Refs. [37] and [42]. The final state with the extra weakly-screened quasi-core hole Ce 5p 1 can probably be explained by the Ce 4+ ion close environment structure. Indeed, if CeO 2 (CeO 2 1/2 (O 1s)) concentration decreases and CeO 3 (CeO 3 1/2 (C 3s)) concentration increases [43], the feature associated with the Ce 5p 1 hole in the XPS spectrum decreases (see, e.g., Fig. 3).

The O 1s XPS spectrum of sample AP1 consists of the primary sharp (I(O 1s) = 1.0 eV) peak at 529.4 eV and a widened (I(O 1s) = 2.0 eV) feature at 531.7 eV of 26% intensity associated with hydroxyl groups (Fig. 8a). With Eq. (3) [66] in mind:

\[
R_{\text{O}} - \text{nm} = 2.27(E_0 - 519.4)^{-1}
\]

even one can evaluate a distance between an element and oxygen for the Ce–O corresponding to E 0 (∆Eg(O 1s) = 529.4 eV as \(R_{\text{O}} = 0.227\) nm, and that corresponding to E 0 (O 1s) = 531.7 eV – as \(R_{\text{O}} = 0.185\) nm. The value of \(R_{\text{O}} = 0.227\) nm with an accuracy of 3% agrees with the value of 0.2344 for a CeO 2 from the crystallographic data in Ref. [44]. The oxygen coefficient \(x = 2.0\) (CeO 2) for sample AP1 found on the basis of the O 1s primary peak intensity and the Ce 3d intensity and the corresponding sensitivity coefficients (see Section 2) is in a qualitative agreement with the expected value of 2 for CeO 2 (Table 3). In the cases of bulk samples AP4 and AP5 the oxygen coefficients exceed significantly the expected value (Table 3). In this case this technique does not allow a correct determination of the oxygen coefficient, as it was shown for uranium oxides UO 2 [7,20]. In the valence band XPS spectrum of sample AP1 (Table 2), which agrees with the data of Refs. [7] and [20]. For sample AP3 more significant changes were observed due to the presence of Ce 3+ ions [7,20]. In the valence band XPS spectrum of sample AP3 the strong growth of the Ce 4f peak at 2.0 eV was observed (Fig. 3b). This agrees with the photoelectron spectrum of CeO 2 obtained by Ar + etching of the surface of CeO 2, which exhibits the Ce 4f peak at 2.0 eV [55]. For sample AP2 the oxygen

### Table 3

| Sample | Ce4+ | Ce3+ | x | \(n_{\text{Ce}}\) |
|--------|------|------|---|-----------------|
| AP1    | 97   | 3    | 2.0 | 0.03             |
| AP2g   | 87   | 13   | 1.9 | 0.08             |
| AP3g   | 29   | 71   | 1.7 | 0.04             |
| AP4g   | 96   | 4    | 2.7 | 0.03             |
| AP5g   | 92   | 8    | 2.6 | 0.04             |
| AP5    | 98   | 2    | 2.5 | 0.03             |

a Ionic composition Ce4+ and Ce3+ (%), found from Eqs. (1) and (2).

b Oxygen coefficient \(x\) in CeO 2 found using the primary O 1s intensity.

c Evaluation of the number of the Ce 4f electrons per one Ce atom was done on the basis of the Ce 4f and Ce 5s XPS intensities taking into account the satellites and with photoionization cross-section in mind [61,62].
coefficient decreases to $x = 1.9$ due to the presence of Ce$^{3+}$ ions (Table 3). An increase of the Ce 4f intensity in the XPS spectrum of sample AP3g relative to that of sample AP1 can be explained by an increase of the number of the Ce$^{3+}$ (4f$^5$) ions in sample AP3g, which also results in the Ce 5s and Ce 4s peaks widening due to the multiplet splitting (Table 2). However, this splitting is absent from the spectra of Ce$^{4+}$ ions [67]. The vanishing of the satellite at 6.9 eV in the Ce 5s spectrum and complication of the IVMO spectrum can be explained by the destruction of the CeO$_2$ (CaF$_2$) structure [43].

The O 1s primary peak of sample AP3g appears 0.8 eV shifted and widened, an extra feature at 531.8 eV was attributed to oxygen from the Si substrate (Fig. 8b). This shift of the primary O 1s peak takes place due to the CeO$_2$ $\rightarrow$ Ce$_2$O$_3$ transition [55,57]. Since $E_b$ (O 1s) = 530.2 eV for sample AP3g (Table 2), with Eq. (3) in mind one can evaluate the mean interatomic distance $R_{\text{Ce-O}}$ in sample AP3g as 0.210 nm, which is significantly lower than $R_{\text{Ce-O}} = 0.227$ nm in sample AP1. This indicates that the irradiation changes dramatically the CeO$_2$ structure and leads to a decrease of the $R_{\text{Ce-O}}$, which is significantly lower than the mean interatomic distance $R_{\text{Ce-O}} = 0.2505$ nm (in the nearest environment of Ce in Ce$_2$O$_3$ there are 3 atoms of oxygen at a distance of 0.2339 nm for the first oxygen atom, 0.2434 nm for the second oxygen atom, and 0.2694 nm for the third oxygen atom) in Ce$_2$O$_3$ [40,68].

The core-level, in particular the Ce 3d, XPS spectrum of sample AP3g exhibits significant changes after irradiation (Fig. 2b). The Ce$^{4+}$ charge transfer- (2, 5) and shake-up- (3, 6) related satellite intensities drops, while the intensity of satellites related to the Ce$^{3+}$ charge transfer ($\Delta E_m$ (Ce 3d$_{5/2}$) = 3.7 eV) significantly grows. This indicates a decrease of the Ce$^{4+}$ concentration and a growth of the Ce$^{3+}$ concentration. Earlier, irradiation of thin film and bulk samples [7,20] of CeO$_2$ with 200 MeV Xe ions to a fluence of $10^{14}$ ions/cm$^2$ caused fewer changes in the Ce 3d spectral structure. Much fewer changes were also observed in the spectra of the bulk samples of cerium dioxide after irradiation (AP4g, AP5g) (Tables 2 and 3), which agrees with the data in Ref. [7].

### 3.4. Ionic composition of CeO$_{2-x}$ oxides

The ionic composition (Ce$^{4+}$ and Ce$^{3+}$) on the surface of the studied samples found by Eqs. (1) and (2) with the calibration coefficient $\alpha_0 = 2.0$ within the measurement error of $\pm 5\%$ (Table 3) agrees with the data in Ref. [35]. The obtained results show that the surface of sample AP1 contains 97% of Ce$^{4+}$ and 3% of Ce$^{3+}$, 2.0 atoms of oxygen for CeO$_2$ and 0.54 atoms of oxygen from hydroxyl groups. The 3% concentration of Ce$^{3+}$ on the surface of sample AP1 (Table 3) agrees with the number of Ce-4f electrons per one cerium atom being 0.03, which was found for Ce 4f and Ce 5s intensities taking into account satellites and with photofragmentation cross-sections in mind [61,62]. For samples AP1, AP2g, and AP3g a correlation of the Ce$^{4+}$ concentration with the oxygen coefficient $x$ in CeO$_2$ and the number of the Ce 4f electrons $n_{\text{e4f}}$ was observed (Table 3).

In the $^{129}$Xe$^{23+}$ irradiated sample AP2g the Ce$^{3+}$ concentration grew up to 13%, and the oxygen coefficient decreased to 1.9 compared to sample AP1 (Table 3). This agrees with the data in Ref. [20]. An increase of Ce$^{4+}$ ions concentration to 71% was observed for irradiated sample AP3g. Such severe radiation damage can be explained by its low thickness. As noted, the CeO$_2$ samples were studied with the XRD, SEM and dissolution experiments in Ref. [19]. According to our evaluation with the dissolution and XPS data in mind, the film in sample AP2g is nominally about 20 times thicker than the film in sample AP3g. This agrees with the SEM data that show that the film in sample AP3g fragmented (the film in sample AP2g developed pores – see Fig. 3 in Ref. [19], the film in sample AP3g fragmented – see Fig. 4 in Ref. [19]). As a result, the XPS spectrum of sample AP3g exhibits intense Si 2s, 2p peaks, which were not observed in the XPS spectrum of samples AP1 (Fig. 1) and AP2g. Silicon-related features were not observed in the XPS of AP2g, since the spectra were taken from a continuous film region without pores (see Fig. 3 in Ref. [19]).

The valence and core-electron XPS spectrum of bulk samples AP4 and AP5 do not much differ from the corresponding spectra of sample AP1 (Fig. 3a, Table 2). The ion irradiation does not bring significant changes in their spectral structures (Table 3). This can be explained by the presence of excess oxygen on the surface that can oxidize the Ce$^{3+}$ ions forming under the $^{129}$Xe$^{23+}$ irradiation. The spectral structure qualitatively show that the irradiated samples (AP4g and AP5g) contain more Ce$^{3+}$ ions than the unirradiated ones (AP4 and AP5) (Table 3). This agrees with the data of other authors in Ref. [7]. In addition, the XPS measurements performed in Ref. [69] on unirradiated and Xe ion irradiated (under the same conditions) bulk samples of UO$_2$ indicated that the samples were subjected to significant surface oxidation, since the samples were cut and stored under an ambient air atmosphere, and surface oxidation has masked potential ion irradiation effects. Hence, no noticeable difference in the uranium ionic surface composition was observed between the irradiated and unirradiated samples.

### 4. Conclusions

High precision X-ray photoelectron spectra of the single crystal thin film (250 nm) CeO$_2$ on a silicon substrate (sample AP1) and...
the polycrystalline CeO$_2$ fused pellets (AP4 and AP5) were taken in a wide binding energy range of 0–1250 eV.

It was shown that in the spectra of the inner Ce 3p$_{2/3}$, 4s, 4p, 4d, 5s electrons a complex structure forms which is linked mainly with the multielectron excitation. One of the final states of Ce$^{4+}$ ion, formed by photoemission of an electron, contains a vacancy Ce 5p$^1$ in the Ce 5p orbital. This vacancy is virtually an inner vacancy and only weakly screened by the surrounding electrons. It results in intense lines in the spectrum which are unusually strongly shifted by ~14–16 eV toward higher binding energies from the primary spectra lines.

The main cerium state in the film of sample AP1 was found to be Ce$^{4+}$(4$f^0$). The Xe ion irradiation of the films (AP2g and AP3g) and bulk samples (AP4g and AP5g) was found to increase the concentration of the Ce$^{3+}$(4$f^1$) ions containing the unbound Ce 4f electrons manifested as a corresponding peak in the XPS spectra near the Fermi level. On the basis of the spectrum structure, in particular of the Ce 3d-electrons, the cerium ionic composition (Ce$^{3+}$ and Ce$^{4+}$) of the samples was determined. The effect of the Xe ion irradiation on the ionic composition was more pronounced for the thin film rather than bulk samples.

Declarations of interest

None.

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