

Cm(III) Sorption onto Sapphire (α -Al₂O₃) Single Crystals

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In the present study, Cm(III) sorption onto different crystal planes (018), (104), (012), (110), and (001) of sapphire single crystals (area 1 cm²) is investigated at low Cm(III) concentrations and at pH 4.5 and 5.1 by time-resolved laser fluorescence spectroscopy (TRLFS), X-ray photoelectron spectroscopy (XPS), α -spectrometry, and autoradiography. A homogeneous Cm(III) distribution on the sapphire surfaces is demonstrated by autoradiography for all samples. Sorbed Cm(III) concentrations are in the range 2×10^{-12} – 7×10^{-11} mol/cm² or 0.02–0.4 atoms/nm². TRLFS and XPS spectra of sufficient intensity are obtained for all samples, proving the sensitivity of these techniques and their applicability at very low Cm(III) concentrations. TRLFS spectra of Cm(III) sorbed onto the (001) surface show distinct differences with regard to peak position and fluorescence lifetime compared to those obtained for the other four crystal planes. Similar information is available from XPS. The extent of Cm(III) sorption differs for the individual crystal planes, with the highest sorption taking place at the (001) orientation and the lowest at the (018) orientation. Similar TRLFS spectra for Cm(III) sorbed at the (001) plane and onto colloidal γ -Al₂O₃ suggest the presence of similar surface species. Variations in the TRLFS and XPS spectra for Cm(III) sorbed at the (001) plane after high vacuum treatment and after water contact suggest an important influence of surface relaxation processes on the surface properties. Such an effect is much less pronounced for the other sapphire crystal planes.

Introduction

Mechanistic insight into radionuclide interaction with mineral surfaces is of great importance for performance assessment of nuclear waste repositories. Besides retardation processes such as sorption, precipitation, and incorporation reactions at mineral surfaces also an enhanced radionuclide transport via attachment to mobile colloidal phases has to be considered. During past years a lot of studies have been described in the literature dealing with radionuclide sorption onto a multitude of more or less well characterized minerals.^{1–11} For a fundamental understanding of sorption/incorporation processes and a reliable thermodynamic description by, e.g., surface complexation models, all relevant processes have to be identified and quantified. A major point in this respect is the detailed knowledge of the properties and constitution of the reactive mineral surface and the nature, distribution, and concentration of surface sites which is not available or is available only in a limited way for most of the selected minerals. An auspicious possibility to gain deeper insight into processes at the mineral surface is the use of single-crystal surfaces.^{9–11} The main advantage of using single crystals is the possibility of investigating the metal ion sorption on various well-characterized and clearly defined crystal plane surfaces. Due to their low roughness, the availability of different crystal planes and dimensions, and their suitability for performing time-resolved laser fluorescence spectroscopic studies, sapphire (α -Al₂O₃) single crystals were selected for this study. α -Al₂O₃ is taken as a model mineral for trivalent iron oxides and other Al-containing minerals in nature such as clays and gibbsite which are of great importance for metal ion sorption under natural conditions.

In the present paper, first results obtained for the spectroscopic characterization of Cm(III), taken as a model for other trivalent

actinides, sorbed onto five different crystal planes of sapphire (001), (110), (104), (012), and (018) are presented. Time-resolved laser fluorescence spectroscopy (TRLFS), X-ray photoelectron spectroscopy (XPS), α -spectrometry, and autoradiography are used for the experiments. The findings are compared with results from earlier studies on Cm(III) sorption onto colloidal γ -Al₂O₃ particles.^{2,3} On the basis of crystallographic considerations, Barrón and Torrent¹² calculated the oxide/hydroxide density on various hematite surfaces (Table 1). As hematite is isostructural to sapphire,¹¹ we assume those data are applicable to the sapphire surfaces. Surface oxide and hydroxyl groups differ in type and concentration for the different surface planes and thus should have an influence on Cm(III) reactions at the sapphire surface/water interface.

Properties of Sapphire Single-Crystal Surfaces. A number of papers deal with the surface properties of sapphire single crystals of different orientations and their reaction with water in order to understand the reactivity of natural and synthetic aluminum-containing oxides.^{13–24} The clean unhydroxylated (001) surface is supposed to be terminated by a single aluminum layer in which the terminating Al atoms are 3-fold coordinated by the underlying oxygen atoms and are significantly relaxed toward the bulk.^{14,15,18,19} Due to their low coordination number, the Al atoms at the surface are very reactive toward basic ligands such as water.^{20,25–27} According to Wang et al.,¹⁸ the metal-terminated (001) surface is relatively stable across the range of a physically realistic oxygen chemical potential. An oxygen-terminated surface becomes stable only if hydrogen is present on the surface.¹⁸ Liu et al.²⁵ studied the reaction of water vapor with a (001) surface using synchrotron-based photoemission spectroscopy (PES). Below a threshold of ca. 1 Torr, the dissociative chemisorption of water occurs mainly at defect sites; above the threshold extensive hydroxylation was found, increasing with increasing exposure times. Eng et al.¹³ also mentioned

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TABLE 1: Surface Oxide/Hydroxide Densities for Singly, Doubly, and Triply Coordinated Oxygen Atoms Calculated for Various Hematite Surfaces Identical to Those Used in the Present Study with Isostructural Sapphire Single Crystals^a

surface	singly coordinated (groups nm ⁻²)	doubly coordinated (groups nm ⁻²)	triply coordinated (groups nm ⁻²)	contiguous singly coordinated (group pairs nm ⁻²)
(110)	5.0	5.0	5.0	2.5
(012)	7.3		7.3	3.7
(104)	5.3	5.3	5.3	
(018)		6.3	3.2	
(001)		13.7		

^a Contiguous singly coordinated groups are also given at a distance of ca. 0.3 nm. Data were taken from Barrón and Torrent.¹²

a water vapor pressure of about 1 Torr being sufficient to fully hydroxylate the (001) surface. The structure of the fully hydrated surface investigated by crystal truncation rod diffraction is oxygen terminated with doubly coordinated surface oxygens and with a 53% contracted double Al layer directly below. The structure was identified as an intermediate between α -Al₂O₃ and γ -Al(OH)₃ (gibbsite).¹³ The proposed model for the structure of the hydrated/oxygenated (1102) orientation (identical to (012)) published by Trainor et al.²⁴ implies the presence of surface oxygen atoms which are singly, doubly, and triply coordinated with aluminum.

Sorption of different metal ions onto sapphire single crystals is described in the literature.^{10,11,28,29} Pb(II) sorption onto the (001) and (012) surface is published by Trainor et al.¹⁰ Taking into account the empirical model of Hiemstra et al.,³⁰ they predict a near-negligible surface charge for the (001) surface over a wide range (pH 2–10), whereas the (1102) (respectively (012)) surface is positively charged at pH < 8. Experiments performed at pH 4.5 exhibit a higher sorption onto the (012) surface compared to (001). There are spectroscopic hints that Pb(II) is sorbed as an inner-sphere complex on the (012) surface and as an outer-sphere complex onto the (001) surface.²⁹ On the other hand, Co(II) forms inner-sphere complexes on both surfaces as could be shown using grazing-incidence X-ray absorption fine structure spectroscopy.³¹ U(VI) sorption onto the (110) surface using the same experimental method is interpreted as a bidentate inner-sphere binding at the AlO₆ octahedra edge sites (doubly coordinated oxygen atoms).¹¹

Experimental Section

Sapphire single crystals with five different surfaces, (001), (110), (104), (012), and (018), and a dimension of 1 × 1 cm were used for the Cm(III) sorption experiments. The one-side epipolished single crystals (TBL Kelpin, Neuhausen, Germany) with a specified thickness of 0.5 mm, an orientation tolerance <0.5° (normally 0.3°), a surface roughness <2 nm, and a surface flatness <1 μ m/cm were cleaned by two different procedures prior to sorption experiments to remove adherent surface impurities: (1) washing only with Milli-Q water; (2) washing with acetone overnight, then washing with ethanol for 2 h, and finally rinsing several times with Milli-Q water. No ultrasonic treatment was used in either case. The yield of the cleaning procedure was checked by subsequent XPS analyses. A ²⁴⁸Cm(III) (*t*_{1/2} = 3.49 × 10⁵ years) stock solution with a concentration of 8 × 10⁻⁴ M stored in concentrated HCl was used for this study and consisted of 97.2% curium-248, 2.8% curium-246, and less than 0.01% curium-244. All experiments were performed in a glovebox under argon atmosphere to avoid

any influence of carbonate. For sorption experiments 10 mL of a 6.5 × 10⁻⁷–1.3 × 10⁻⁶ mol/L Cm(III) solution with an ionic strength of 0.1 M NaClO₄ was pH adjusted by adding CO₂-free sodium hydroxide solutions (J. T. Baker B. V., Deventer, Holland) and then divided into five different precleaned polypropylene wide-mouth jars with a volume of 10 mL each. Two different sets of experiments were performed with all sapphire surfaces: one at pH 4.5 with single crystals washed only with Milli-Q water prior to sorption experiments (at 1.3 × 10⁻⁶ mol/L Cm(III)_{tot}) and the other one at pH 5.1 with a more extended purification procedure of the single crystals (see description above) at 6.5 × 10⁻⁷ mol/L Cm(III)_{tot}. The experimental pH range was selected on the basis of previous sorption studies on γ -Al₂O₃ colloids^{2,3} where significant Eu(III), Am(III), and Cm(III) sorption starts at pH ≥ 4. A second reason was to keep the system as simple as possible. Cm(III) is present in solution only as the free aquo ion at pH ≤ 6, and neither hydrolysis nor carbonate complexation plays an important role in Cm(III) aqueous speciation under these experimental conditions.³² For sorption studies, single crystals were placed carefully on the solution surface with the polished side down. By this procedure the polished side was floating on the solution surface due to surface tension and the rough back side was not moistened. After a contact time of 2–3 days, the crystals were removed from solution.

TRLFS measurements were performed using a pulsed Nd:YAG pumped dye laser system (Continuum, Powerlite 9030, ND 6000) at a repetition rate of 10 Hz. Some efforts had to be made to measure the very low Cm(III) concentrations at the sapphire surface: The single crystals were illuminated by the pulsed laser light under an angle of 40° at a constant excitation wavelength of 396.6 nm (laser dye Exalite 398) and a laser energy of 4–5 mJ. Perpendicular to the laser beam and very close above the single crystals, a circular glass fiber bundle with a diameter of 3.2 mm and an effective area of about 4.2–5.3 mm² (the exact number of 70 μ m fibers used in the fiber bundle is not known) was fixed. To avoid an influence of reflected or scattered light from the laser and to decrease the background signal, a long-wave pass filter (10 LWF-500, Newport) was mounted in front of the fiber. Furthermore, an Al foil was located below the single crystals to increase the Cm(III) fluorescence intensity due to reflection of the fluorescence light emitted in the direction opposite to the fiber. For the first sorption experiments at pH 4.5 a glass fiber bundle with an effective diameter of only 1 mm² and no Al foil was used, resulting in a lower sensitivity by a factor of about 20 and a higher noise level of the fluorescence spectra. The collected fluorescence emission was detected by an optical multichannel analyzer consisting of a polychromator (Chromex 250 is) with a 1200 lines/mm grating. The emission spectra of Cm(III) sorbed on single crystals were recorded 1 μ s after the laser pulse in the range 580–620 nm and a time window of 1 ms. For lifetime measurements the time delay between laser pulse and camera gating was scanned with time intervals between 10 and 15 μ s.

The elemental composition on the sapphire surface was determined by XPS. The XPS spectrometer used was a PHI Model 5600ci (7 × 10⁻⁸ Pa base pressure) with a multichannel detector. XPS spectra were acquired by use of monochromatic Al K α (1486.6 eV, 200 W source power) X-ray excitation in combination with an electron flood gun for surface neutralization. High-resolution scans of elemental lines were recorded at 23.5 eV pass energy of the hemispherical capacitor analyzer, which yields a full width at half-maximum (FWHM) of the Ag 4d_{5/2} line of 0.73 eV. The energy scale of the spectrometer was

TABLE 2: Quantification of Cm(III) Sorption onto Various Single-Crystal Surfaces of Sapphire at pH 4.5 and 5.1 without Consideration of Edge Site Sorption^a

face	α -spectrometry				autoradiography		TRLFS	
	$c(\text{Cm(III)}) (\text{mol}/\text{cm}^{-2})$		net sum (%)		net sum (%)		net sum (%)	
	pH 4.5	pH 5.1	pH 4.5	pH 5.1	pH 4.5	pH 5.1	pH 4.5	pH 5.1
(018)	2.62×10^{-12}	2.81×10^{-12}	2.87	4.12	2.27	2.92	5.81	7.03
(104)	5.84×10^{-12}	4.74×10^{-12}	6.39	6.95	5.09	6.22	17.00	28.28
(012)	7.69×10^{-12}	1.04×10^{-11}	8.41	15.19	9.39	17.66	8.56	13.57
(110)	8.91×10^{-12}	7.28×10^{-12}	9.75	10.68	11.42	9.49	5.00	8.05
(001)	6.63×10^{-11}	4.30×10^{-11}	72.58	63.06	71.82	63.71	63.62	43.07

^a Besides absolute values from α -spectrometry, also relative values (net sum is the intensity/concentration on each surface as a fraction of the total intensity/concentration) are given from α -spectrometry, autoradiography, and TRLFS to compare the different methods.

calibrated with the Cu 2p_{3/2}, Ag 3d_{5/2}, and Au 4f_{7/2} lines³³ of pure and Ar⁺ sputter cleaned metal foils. The binding energies of elemental lines are charge referenced to the C 1s line of adventitious hydrocarbon at a binding energy (BE) of 284.8 eV.

Spectra of Cm(III) sorbed onto a sapphire (001) surface acquired using first monochromatic X-rays, followed by examination with Al K α X-ray irradiation (300 W source power, sample distance 10 mm, 140 min) and subsequent analysis by monochromatic X-rays, were compared to spectra of Cm(III) sorbed onto a (110) surface of sapphire acquired under identical conditions.

Quantification of sorbed Cm(III) was done by α -spectrometry (Model 7401, Canberra) with a PIPS (passivated, ion-implanted planar silicon) detector of 450 mm² area. Acquisition time was fixed to 1000 min at a vacuum <5 Pa.

For autoradiography experiments the phosphor storage screen technology was used (Cyclone, Storage Phosphor System, Packard Instrument Company, USA). The measurement period for single crystals was about 3 h. Radiation was stored in reusable phosphor screens of BaFBr:Eu²⁺ crystals as defect energy. For reading out, the screens were scanned with a red laser and the stored crystal defects emitted blue light which is detected. The main advantages compared to films are higher sensitivity and enhanced linear dynamic range. The lateral resolution is 600 dpi, equal to about 40 μm .

Results and Discussion

Cm(III) Coverage at the α -Al₂O₃ Surface. XPS investigations on untreated sapphire single crystals reveal impurities at the surface consisting of F, Na, Ca, S, Cu, and Zn and large amounts of carbon. The carbon contamination possibly consists of residues from adhesion polymer foils protecting the surface during the cutting process. Washing with organic solvents (according to the purification procedure with acetone and ethanol described in the Experimental Section) reduces the carbon contamination considerably. Subsequent washing with Milli-Q water removes remaining inorganic contamination, and only minor amounts of F could be detected by XPS.

For both sets of experiments at pH 4.5 and 5.1, the TRLFS spectra normalized to the same peak height are absolutely identical irrespective of the purification procedure applied. Thus, the surface contaminations obviously do not exert a significant effect on the Cm(III) speciation.

Autoradiography was performed to check for the homogeneity of the Cm(III) distribution at the single-crystal surfaces. Considering the lateral resolution of the method, Cm(III) is found to be homogeneously distributed at the surfaces after both cleaning procedures. Cm(III) sorption is, however, clearly increased at the sheet edges. Edge site sorption comprises 15–70% of the totally sorbed Cm(III). Edge site sorption was not further investigated by all experimental methods used in

this study. This was done by masking out these areas using apertures and/or by the low spatial dimensions of the laser and X-ray beam in TRLFS and XPS, respectively. It is obvious from the study that we have large differences between the Cm(III) coverage at the different plane surfaces (without edge sites). The (001) surface exhibits the highest α -activity at the plane surface (without considering edge site sorption) and the lowest values are found for the (104) and (018) planes. As we did not calibrate the method, only relative surface coverage can be given for the different planes (see Table 2). Relative surface coverages are also deduced from the fluorescence intensities measured by TRLFS. Due to the unknown fluorescence intensity factors for the individual species (which can be estimated by considering quantitative sorption data) formed at the different planes, those data are somewhat uncertain and, therefore, show deviations from the other data.

Quantitative surface coverage data were obtained by α -spectrometry. Single crystal sheets were covered with self-made paper pockets with an aperture of 5.5 mm to suppress the influence of Cm(III) enriched at the sheet edges. The results are summarized in Table 2 as absolute values and as relative values (net sum) to allow for comparison with autoradiography and TRLFS data. Cm(III) sorption data vary widely for the different crystal planes: by a factor of 25 between coverages of 2.6×10^{-12} and 6.6×10^{-11} mol/cm² at pH 4.5 and by a factor of 15 in a range from 2.8×10^{-12} to 4.3×10^{-11} mol/cm² at pH 5.1. The (001) surface shows the highest and the (018) surface shows the lowest Cm(III) loading at both pH values and after both purification procedures, respectively. Comparison of results from α -spectrometry and autoradiography (Table 2) shows good agreement for both methods. Data from TRLFS differ somewhat more especially for the (104) surface due to unknown fluorescence intensity factors as already mentioned. As follows from all experimental methods used, TRLFS, autoradiography, and α -spectrometry, there is no clear visible hint of an influence of the different sapphire purification procedures on the Cm(III) sorption onto these surfaces.

From α -spectrometry a Cm(III) concentration in the range of 0.016–0.40 atoms/nm² can be calculated for the different single-crystal surfaces. Taking into account a surface site density calculated by Barrón and Torrent¹² between about 5 and 15 sites/nm² (Table 1), the maximum surface coverage with Cm(III) is in the range of 3–10% of available sites. In all experiments less than 3% of the total Cm(III) is sorbed. To avoid saturation effects of the surface binding sites at increased pH, the total Cm(III) concentration at pH 5.1 was halved as compared to pH 4.5 (see Experimental Section).

Comparing the Cm(III) sorption on all sapphire single crystal planes at pH 4.5 and 5.1 with that on γ -Al₂O₃ colloids determined in an earlier study for Eu(III) and Am(III)³ reveals that Cm(III) sorption on the single crystals is conspicuously

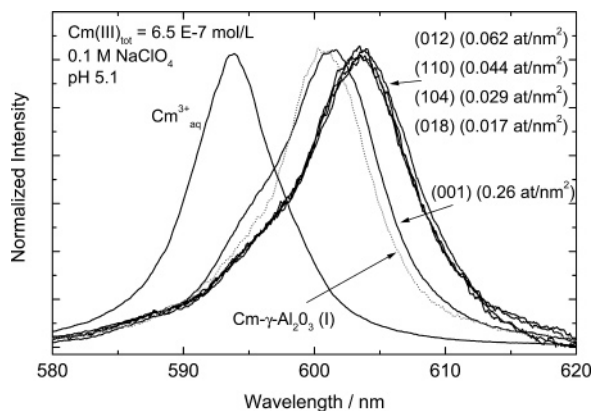


Figure 1. TRLFS spectra for the Cm(III) sorption onto different sapphire single crystals (001), (110), (012), (104), and (018) at pH 5.1 and 0.1 M NaClO₄ normalized to the same peak height. Cm(III) surface concentrations measured by α -spectrometry are added in parentheses in atoms/nm². Also, the spectra for the unsorbed free Cm³⁺ aquo ion and for the first Cm(III) sorption species onto γ -Al₂O₃ derived by peak deconvolution at similar pHs⁴ are included.

enhanced by 2 or 3 orders of magnitude. A possible explanation for this observation may be a change in the acid–base properties of single-crystal surface hydroxyl groups as compared to the colloidal surfaces, resulting in a decrease of the point of zero charge (PZC) as already mentioned in the literature. Franks and Meagher³⁴ found values between pH 5.0 and 6.0 for four different orientations. Other authors partly report even lower values down to pH 3.³⁵ The decrease in PZC for single-crystal surfaces is not yet fully understood³⁵ and may also be due to contamination by, e.g., silicates. PZC of γ -Al₂O₃ colloids is significantly higher and was found at pH 8.6 by titration and microelectrophoresis³ and, therefore, lies within the range of published values (pH 8.0–9.5).³⁴ As can be demonstrated by a scoping calculation, a decrease of PZC by about 3–4 pH units may explain the increased Cm(III) sorption at the sapphire single-crystal surface as compared with that at γ -Al₂O₃.

Spectroscopic Study. A relatively high background intensity caused by a variable and/or a nonhomogeneous chromium contamination in the bulk of the single crystals was observed. This is in agreement with other publications where in nominally pure corundum crystals also Cr(III) impurities could be found.³⁶ Cr(III) spectra with a sharp and very intensive peak at 694.3 nm and long lifetimes are well-known from the ruby laser (Al₂O₃:Cr). They generate an increase in the background signal in a spectral range between 580 and 620 nm, where we measure the Cm(III) fluorescence. At higher Cm(III) fluorescence intensities, as is the case in Figure 1, the Cr background subtraction has only minor effects on the pure Cm(III) spectra. At low Cm(III) concentration when background intensity is similar to that of the Cm(III) fluorescence or even higher (i.e., at lifetime measurements using higher delay times) background subtraction is more sophisticated. This is due to the fact that the Cr fluorescence intensity varies not only for the different crystal surfaces but also for different crystals for the same surface. Even 90° rotation of the crystals on the sample holder influences the measured Cr intensity. Besides varying or inhomogeneous Cr distributions within the respective crystals, also polarization effects can be a possible explanation for the different Cr background intensities.³⁷ Therefore, a peak deconvolution had to be performed taking into account the known spectra of the pure Cm(III) and the Cr background.

The normalized Cm(III) spectra for the sorption onto sapphire single crystals at pH 5.1 are shown in Figure 1. Fluorescence induced by Cr is subtracted from the raw data. The red shift of

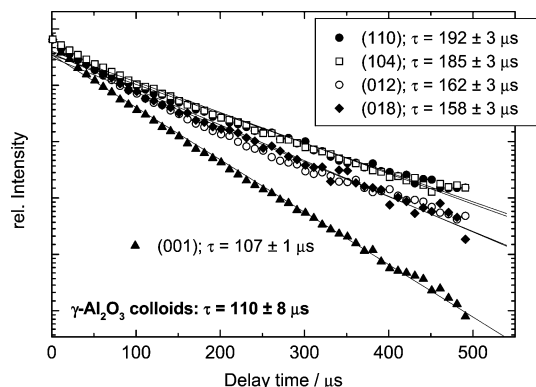


Figure 2. Fluorescence lifetimes of sorbed Cm(III) onto sapphire single crystals of different orientations.

the fluorescence emission is caused by a change in the ligand field of the Cm(III) first coordination sphere, and thus, it is evident that Cm(III) forms inner-sphere complexes at the sapphire surface.³⁸ In the case of outer-sphere complex formation where Cm(III) keeps its complete hydration sphere, TRLFS spectra are not affected and closely resemble the spectrum of the Cm(III) aquo ion. This has been clearly demonstrated for the Cm(III) sorption onto clay material where outer-sphere sorption on interlayer sites prevail at low pH values.³⁹

Residual Cm(III) aquo ions on single-crystal surfaces dissolved in the surface adhering solution film could not be identified. A comparative experiment performed with a 2 μ L drop of an acidic Cm³⁺ solution (pH 1) shows, as expected, the peak position and fluorescence lifetime of the emission band corresponding to those of the Cm(III) aquo ion. In that case the Cm(III) ion keeps its complete hydration sphere and no interaction with the single-crystal surface is observed. Figure 1 shows that the spectra for Cm(III) sorbed onto the (001) surface (peak position $\lambda_{\text{max}} = 601.3$ nm) differ significantly from the spectra of the other four surface species, which are almost identical ($\lambda_{\text{max}} = 603.6$ nm). Similar spectra obtained for Cm(III) sorbed at the same pH at the α -Al₂O₃ (001) plane and the γ -Al₂O₃ colloid surface indicate comparable sorption mechanisms and surface species⁴ (Figure 1).

The time dependent fluorescence intensities for the different samples are plotted in Figure 2 for pH 5.1. Almost identical results are obtained at pH 4.5. For all surfaces a monoexponential decay is observed, suggesting the presence of only one Cm(III) species. The fluorescence lifetime for the Cm(III) sorbed at the (001) surface differs from those obtained for the other surfaces. The value of 107 ± 1 μ s is again very close to the lifetime of about 110 μ s observed for the Cm(III) sorption onto γ -Al₂O₃ colloids.² By applying the empirical correlation of Kimura,⁴⁰ we can derive from the fluorescence lifetime the presence of ca. 5 H₂O molecules or OH[−] ions in the inner coordination sphere of Cm(III). The lifetimes for the four other crystal planes lie in the range 158–192 μ s, corresponding to 3.2–2.5 water/OH[−] molecules in the first hydration sphere. Taking into account the uncertainties based on the background subtraction procedure, the lifetimes for (012), (110), (018), and (104) surfaces are relatively similar. Emission spectra and lifetimes of samples stored for 2 months in closed jars under aerobic conditions do not show any significant variations and, thus, point to the kinetic stability of the system.

(001) and (110) sapphire crystal planes with Cm(III) sorbed at pH 4.5 were inspected by XPS. Spectra are shown in Figure 3. The binding energy for the Cm 4f_{7/2} electrons at the (110) surface is found to be constant at 473.8 ± 0.1 eV, unaffected by X-ray irradiation and ultra high vacuum (UHV) conditions.

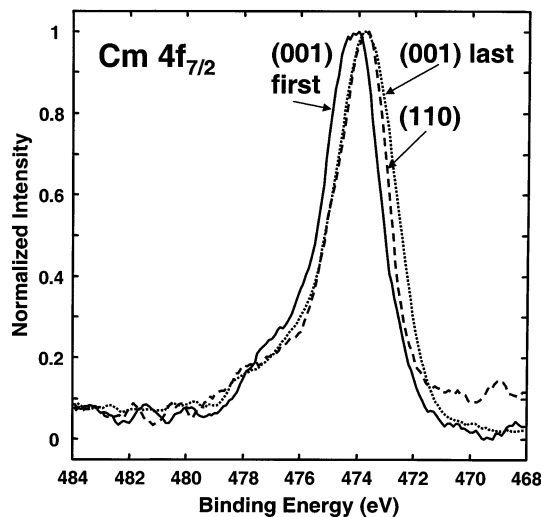


Figure 3. Cm 4f_{7/2} spectra measured by XPS for Cm(III) sorption onto (001) and (110) sapphire single crystal planes. In the case of the (001) surface the first and the last spectrum are shown within an intensive XPS study (large measuring time, high power, etc.). Spectra are smoothed by a 15-point Savitzky–Golay convolution.

Spectra obtained for the (001) surface show a significant change with time upon Al K α X-ray irradiation (300 W, 140 min) under UHV conditions (see Experimental Section). The initial peak at 474.1 ± 0.1 eV moves to lower binding energy and finally ends up at 473.8 ± 0.1 eV, i.e., at the same position found for the Cm(III) bound to the (110) surface. XPS publications on Cm compounds are scarce,^{41–43} but in all cases asymmetric Cm(III) 4f lines with a shoulder on the high binding energy side are observed as found in our spectra. Binding energies of 472.7 ± 0.5 ⁴¹ and 472.4 ± 0.4 eV⁴³ are reported for Cm oxide. Chemical shifts of the 4f_{7/2} lines differ by 2.4 eV for Cm oxide and Cm fluoride³⁹ despite screening of 4f states. Chemical shifts for Cm(III) on sapphire planes differ by only 0.3 eV. Cm 4f_{7/2} is the most intense line of the Cm spectrum at the X-ray energy used. Estimation of line intensity of the unscreened, localized Cm 5f electrons by use of photoionization cross sections⁴⁴ results in 21 times less intensity than for Cm 4f lines. Atomic concentrations of Cm determined by XPS survey spectra are well below 0.1%, and Cm 5f line intensity is expected close to the noise level. In addition, superposition of the Cm 5f spectrum^{45,46} with the valence band of sapphire is expected. As the binding energy inversely correlates with the electron density at the Cm ion, one can conclude that electron density increases in the following direction: Cm(III) (001) plane < Cm(III) (110) plane < CmO_x. Assuming the Cm(III) coordination mainly takes place via oxygen atoms for all those compounds, the XPS data suggest an increase of either the number of oxygen atoms close to the Cm(III) ion or the strength of the Cm(III)–O binding, i.e., a decrease of the bond distance, in the same direction.

Before and after XPS treatment, samples were checked with TRLFS for potential changes. The TRLFS spectra recorded several hours before and 1 day after XPS measurements show, in agreement with the XPS measurements, a shift of the emission band for the Cm(III) bound to the (001) plane. The final spectrum now closely resembles those obtained for the (110), (012), (104), and (018) surfaces (Figure 4a). Storage of the sample in a jar under ambient air for 140 days reveals the reversibility of this shift: After the storage time, the Cm(III) peak appears to be somewhat broader, but the peak position is the same as before XPS analysis (Figure 4b). The peak shift to higher wavelength in the TRLFS spectra for the XPS treated

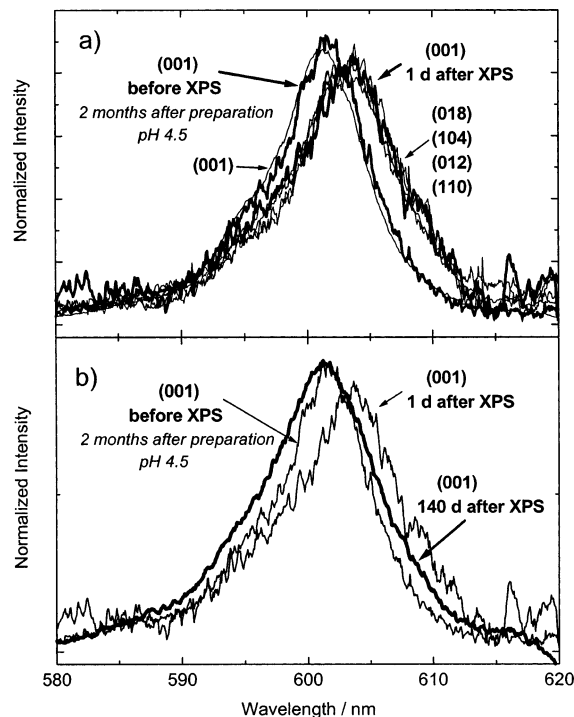


Figure 4. Influence of XPS treatment on TRLFS spectra of Cm(III) sorbed on (001) sapphire surface at pH 4.5. (a) Spectra immediately before and 1 day after XPS measurement. For comparison, the original spectra obtained for all selected surfaces at pH 4.5 are included as thin lines. (b) Spectrum 140 days after XPS treatment is added in bold.

Cm(III) (001) surface sample to the same peak position of the (012), (104), (018), and (110) surfaces points to a higher ligand field splitting due to stronger ligands or due to increasing numbers of coordinating ligand groups after the XPS analysis. Such a finding is consistent with the evaluation of the XPS spectra. Also, the results from the fluorescence lifetime measurements support this assumption: As the Cm(III) tends to have a 9-fold coordination in aqueous systems and the number of water molecules for the sorption onto the (001) surface (lifetime $\tau = 107$ μ s) and onto the four other surfaces (lifetime $\tau = 158$ – 192 μ s) are calculated to be about 5 and 3, respectively, the number of coordinated surface oxygen atoms should be lower for the (001) orientation.

The spectroscopic findings point to the existence of two Cm(III) binding modes at Al₂O₃ surfaces. One is characterized by the presence of a weaker ligand field as indicated by the higher binding energy of the Cm 4f_{7/2} electrons, a lower peak shift in the TRLFS spectra, and a shorter fluorescence lifetime corresponding to five H₂O molecules in the first coordination sphere. That species (called species 1) is observed to be present at the α -Al₂O₃ (001) plane and the colloidal γ -Al₂O₃ surface. The second Cm(III)–Al₂O₃ species is characterized by a lower binding energy of the Cm 4f_{7/2} electrons, a more pronounced red shift of the fluorescence emission spectrum, and a longer fluorescence lifetime corresponding to only three H₂O molecules left in the first coordination sphere. That species (called species 2) is found at the α -Al₂O₃ single-crystal planes other than (001) and develops at the (001) plane after XPS analysis in high vacuum. The transformation of species 1 into species 2 at the (001) plane may be explained by changes in the α -Al₂O₃ surface structure as a consequence of the treatment. The reverse reaction under aerobic conditions points to the rearrangement of the surface due to interaction with water vapor. The extensive hydroxylation of the α -Al₂O₃ (001) crystal plane at water vapor

pressures > 1 Torr concomitant with structural changes toward γ -Al(OH)₃ (gibbsite) at the surface has indeed been observed.¹³ There are a number of indications (unusually high solubility, spectroscopic evidence by TRLFS, thermogravimetric measurements)⁴ that the colloidal γ -Al₂O₃ investigated in earlier Am/Eu/Cm(III) studies is covered by a hydrated amorphous Al(OH)₃ surface layer as a consequence of the extensive washing procedure under various pH conditions. This predication is confirmed by the work of Laiti et al., in which a surface phase transformation of γ -Al₂O₃ in aqueous solutions into bayerite (β -Al(OH)₃) is described.⁴⁷ The existence of hydroxidic surfaces at both the colloidal γ -Al₂O₃ and the hydrated α -Al₂O₃ (001) surface would explain the similarity of TRLFS spectra and the higher Cm(III) surface coverage as compared with the other α -Al₂O₃ crystal planes. Consequently, we assume the presence of a more oxidic surface structure in the cases of the (110), (012), (104), and (018) α -Al₂O₃ surfaces. In case of the (001) surface, this oxidic structure appears to be unstable in the presence of water.

Conclusion

The present study shows that TRLFS and XPS are sufficiently sensitive to characterize surface sorbed Cm(III) species even at low surface coverage. By combination of different experimental methods, a better understanding of the reactions on the water/single-crystal surface interface is achieved. The application of different purification methods did not show a significant influence on Cm(III) TRLFS spectra. The outcome of the study points to the important influence of the surface structure and notably the change of the surface properties due to the contact with water. Oxide surfaces experiencing extensive surface hydroxylation and surface phase transformations and thus the generation of a high surface site density may control the sorption of metal ions in natural systems. To gain a deeper insight into the exact structure of the formed surface species, more experiments in a wider pH range and application of additional spectroscopic techniques such as X-ray absorption spectroscopy are required.

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