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Hydrothermal synthesis, structure, Raman spectroscopy, and self-irradiation studies of $^{248}Cm(IO_3)_3$

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Abstract

The study of curium iodate, $Cm(IO_3)_3$, was undertaken as part of a systematic investigation of the 4*f*- and 5*f*-elements' iodates. The reaction of $^{248}CmCl_3$ with aqueous H_5IO_6 under mild hydrothermal conditions results in the reduction of IO_6^{5-} to IO_3^- anions, and the subsequent formation of $Cm(IO_3)_3$ single crystals. Crystallographic data are: (193 K, Mo$K\alpha$, $\lambda = 0.71073$ Å): monoclinic, space group $P2_1/c$, $a = 7.2014(7)$ Å, $b = 8.5062(9)$ Å, $c = 13.4622(14)$ Å, $\beta = 100.142(2)^\circ$, $V = 811.76(14)$, $Z = 4$, $R(F) = 2.11\%$, $R_w(F_o^2) = 4.43\%$ for 119 parameters with 1917 reflections with $I > 2\sigma(I)$. The structure consists of Cm^{3+} cations bound by iodate anions to form $[Cm(IO_3)_8]$ units, where the local coordination environment around the curium centers can be described as a distorted dodecahedron. There are three crystallographically unique iodate anions within the structure; two iodates bridge between three Cm centers, and one iodate bridges between two Cm centers and has a terminal oxygen atom. The bridging of the curium centers by the iodate anions creates a three-dimensional structure. Three strong Raman bands with comparable intensities were observed at 846, 804, and 760 cm^{-1} and correspond to the I–O symmetric stretching of the three crystallographically distinct iodate ions. The Raman profile suggests a lack of inter-ionic vibrational coupling of the I–O stretching, while intra-ionic coupling provides symmetric and asymmetric components that correspond to each iodate site. Repeated collection of X-ray diffraction data for a crystal of $Cm(IO_3)_3$ over a period of time revealed a gradual expansion of the unit cell from self-irradiation. After 71 days, the new parameters were: $a = 7.2132(7)$ Å, $b = 8.5310(8)$ Å, $c = 13.505(1)$ Å, $\beta = 100.021(2)^\circ$, $V = 818.3(2)$.

Keywords: Curium crystal structure; Actinide iodate; Hydrothermal synthesis; Single crystal Raman spectroscopy; Radiation damage

1. Introduction

The solid-state chemistry of *f*-element iodates has proven to be a remarkably rich area of study, as a consequence of the variability in actinide coordination and the numerous coordination modes of the iodate anion. Owing to the oxidizing nature of iodate ($E = 1.195$ V), uranium, neptunium, and plutonium iodates are found to contain these actinides in their (V) and (VI) oxidation states, and compounds such as $NpO_2(IO_3)$ [1], $AnO_2(IO_3)_2(H_2O)$ (An = U, Np) [2,3], $AnO_2(IO_3)_2 \cdot H_2O$ (An = Np, Pu) [3,4] have been isolated following hydrothermal reactions, and their structures determined. One of the key features of these compounds is that they contain actinides in the form of actinyl AnO_2^{n+} (n = 1 or 2) units, which greatly affects the coordination geometries. Additional ligands must bind approximately perpendicular to the actinyl axis which gives rise to tetragonal, pentagonal, and hexagonal bipyramids for six-, seven-, and eight-coordinate actinides, respectively. Attempts to prepare Am(V) or Am(VI) analogs of these iodates have been unsuccessful and have instead yielded compounds containing Am(III) [5].

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Actinide(III) compounds are often found to parallel the chemistry and structural behaviors of 4*f*-element compounds. Lanthanide iodate chemistry has been well-developed in efforts to prepare novel optoelectronic materials [6–15]. Among the more than 13 families of lanthanide iodates are the anhydrous type I $Ln(IO_3)_3$ compounds that have been identified for the entire lanthanide series, except Pm, as well as for Y [7,10,14b]. These compounds contain classic examples of eight-coordinate, distorted dodecahedral Ln^{3+} cations coordinated by iodate anions. The question arose whether the transplutonium (5*f*-element) iodates would parallel the structural chemistry of the 4*f*-element iodates? Regardless, single crystal structures of transplutonium compounds are rare, and elucidating their structures provides important benchmarks. The only single-crystal structure reported previously for an inorganic Cm compound is that of $CmCl_3$ [16]. In previous studies, the precipitation of curium in tracer quantities from aqueous solutions was accomplished by the addition of iodate [17], but the composition of the products was not determined.

The results reported in this present work were obtained with the rare, longer-lived isotope ^{248}Cm ($t_{1/2} = 3.4 \times 10^5$ yr; 5.08 MeV alpha), which is only available in milligram quantities, thereby making synthesis and growth of single-crystals challenging. The decay of ^{248}Cm involves alpha decay in addition to the neutrons and fission fragments from spontaneous fission. Use of this isotope is critical for single crystal diffraction measurements because the self-irradiation of ^{244}Cm ($t_{1/2} = 18.11$ yr) can cause substantial damage to crystal lattices [16,18,19]. The crystal structures and electronic properties of selected curium compounds are also the subject of a recent density functional theory study [20]. Herein we report the hydrothermal synthesis, single-crystal structure, Raman spectrum, and the self-irradiation effects on $^{248}Cm(IO_3)_3$, which represents the heaviest actinide iodate reported to date.

2. Experimental

2.1. Synthesis of $Cm(IO_3)_3$

The ^{248}Cm (~3% ^{246}Cm) used in this study was obtained as part of the Basic Energy Sciences production program involving the High-Flux Isotope Reactor at Oak Ridge National Laboratory. The H_5IO_6 (98%, Alfa-Aesar) was used as received. The preparation involved mixing 10 μL of 0.12 M Cm^{3+} in 0.10 M HCl and 40 μL of 0.1 M H_5IO_6 in a quartz tube. An unidentified, off-white precipitate initially formed upon mixing of these two solutions. The tube was then flame sealed and placed in a furnace that was subsequently heated to 180 °C, where the reaction/crystallization occurred under an autogenously generated pressure. After 113 h the furnace was cooled at 25 °C/h down to 100 °C, then turned off and allowed to cool to 20 °C. At this point, the tube contained orange/brown crystals of $Cm(IO_3)_3$ as the sole solid product, which were immersed in a colorless mother liquor.

2.2. Crystallographic studies

One of the single crystals of $Cm(IO_3)_3$ ($0.136 \times 0.150 \times 0.188\,mm^3$) was selected, sealed in a capillary, and then analyzed using a Bruker SMART APEX CCD X-ray diffractometer. Intensity measurements were performed using graphite monochromated Mo$K\alpha$ radiation from a sealed tube with a monocapillary collimator. SMART was used for preliminary determination of the cell constants and for data collection control. The intensities and positions of the reflections of a sphere were collected by a combination of three sets of exposure frames. Each set had a different ϕ angle for the crystal and each exposure covered a range of 0.3° in ω. A total of 1800 frames were collected with an exposure time of 30 s per frame.

The determination of integrated intensities and a global cell refinement were performed with the Bruker SAINT (v 6.02) software package using a narrow-frame, integration algorithm. These data files were subsequently treated with a semi-empirical absorption correction using SADABS [21]. The program suite, SHELXTL (v 5.1), was used for space group determination (XPREP), direct methods structure solution (XS), and least-squares refinement (XL) [22]. The final refinements included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Selected crystallographic details are listed in Table 1, and atomic coordinates and equivalent isotropic displacement parameters are given in Table 2. Further details of the crystal structure investigation may be obtained from the Fachinformationzentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 413985.

2.3. Raman spectroscopy

Raman spectroscopy was performed using an argon-ion laser (Coherent, model 306) and a double-meter spectrometer (Jobin-Yvon Ramanor model HG.2S). The resolution of the monochromator at 514.5 nm is 0.5 cm^{-1}. The monochromator is also interfaced with a personal computer; scanning and data collections are controlled by LabSpec (version 3.04) software. Signal detection was acquired with a water-cooled photo-multiplier tube (Hamamatsu R636).

Table 1
Crystallographic data for $Cm(IO_3)_3$

Compound	$^{248}Cm(IO_3)_3$
Formula mass (amu)	772.70
Color and habit	Variable,[a] prism
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 14)
a (Å)	7.2014(7)
b (Å)	8.5062(9)
c (Å)	13.4622(14)
β (°)	100.142(2)
V (Å^3)	811.76(14)
Z	4
T (K)	193
λ (Å)	0.71073
$2\theta_{max}$ (°)	56.62
ρ_{calcd} (g cm^{-3})	6.323
Measured reflections	7842
Unique reflections	2005
R_{int}	0.0243
μ(Mo$K\alpha$) (cm^{-1})	214.76
$R(F)$ for $F_o^2 > 2\sigma(F_o^2)$ [b]	0.0211
$R_w(F_o^2)$[c]	0.0443

[a] The color of the crystals of $Cm(IO_3)_3$ is altered by radiation damage. The crystals change from orange/brown to dark purple and finally to black.

[b] $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$.

[c] $R_w(F_o^2) = [\sum[w(F_o^2 - F_c^2)^2] / \sum wF_o^4]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0000P)^2 + 5.7838P]$ and $P = (F_o^2 + 2F_c^2)/3$.

Table 2
Atomic coordinates and equivalent isotropic displacement parameters for $Cm(IO_3)_3$

Atom (site)	x	y	z	U_{eq} (Å^2)[a]
Cm(1)	0.67612(3)	0.25232(2)	0.144557(15)	0.00729(7)
I(1)	0.32962(5)	0.21222(4)	−0.11271(3)	0.00982(9)
I(2)	0.17094(5)	0.03883(4)	0.14046(3)	0.00805(9)
I(3)	0.77164(5)	0.01582(4)	0.39247(3)	0.00843(9)
O(1)	0.1417(7)	0.1698(6)	−0.0451(4)	0.0199(10)
O(2)	0.5323(6)	0.1687(5)	−0.0168(3)	0.0149(9)
O(3)	0.3325(7)	0.0346(5)	−0.1855(3)	0.0143(9)
O(4)	0.9778(6)	0.1727(5)	0.1303(4)	0.0170(10)
O(5)	0.3559(6)	0.1831(5)	0.1742(3)	0.0137(9)
O(6)	0.1569(6)	−0.0319(5)	0.2652(3)	0.0130(9)
O(7)	0.7425(6)	0.2045(5)	0.3275(3)	0.0137(9)
O(8)	0.8218(6)	0.0721(5)	0.5234(3)	0.0139(9)
O(9)	0.5260(6)	−0.0259(5)	0.3866(3)	0.0139(9)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

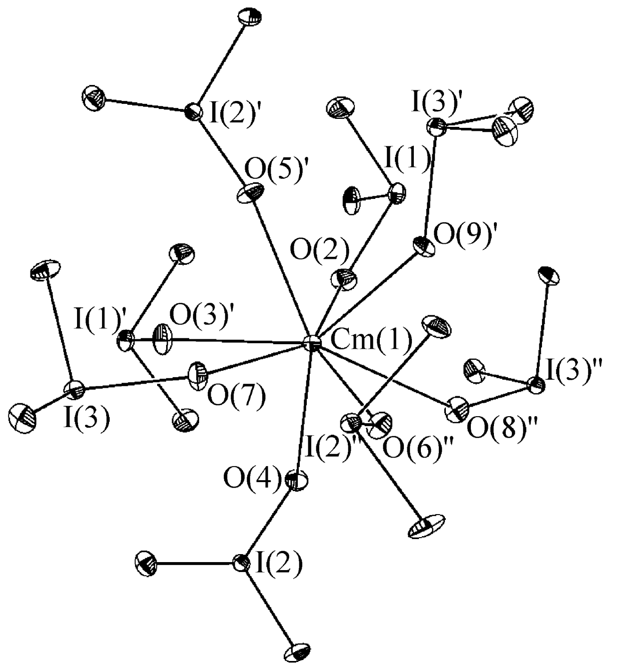

Fig. 1. An illustration of the distorted dodecahedral environment around the Cm^{3+} centers in $Cm(IO_3)_3$. 50% displacement ellipsoids are shown.

3. Results and discussion

3.1. Structure

The structure of $Cm(IO_3)_3$ was determined to be isostructural with that of type I $Gd(IO_3)_3$, which is part of an isostructural series of compounds formed with elements ranging from Ce to Lu (except for Pm) and Y, and is the series of iodate compounds with the most members [7,10,14b]. This structure consists of Cm^{3+} cations bound by iodate anions to create a three-dimensional architecture. The curium centers are bound by eight bridging iodate anions to create a distorted, dodecahedral environment around the Cm^{3+} cations in the $[Cm(IO_3)_8]$ units as shown in Fig. 1.

The Cm–O bond distances range from 2.315(4) to 2.568(4) Å with an average value of 2.431(4) Å. This average value is 0.034(4) Å larger than the average Gd–O bond distance reported in $Gd(IO_3)_3$, and is consistent with Cm^{3+} having a larger ionic radius than Gd^{3+}. The ionic radius of Cm^{3+} is most similar to that of Sm^{3+}, 1.079 Å for coordination number eight, whereas Gd^{3+} has an ionic radius of 1.053 Å (CN = 8) [23]. Thus, the calculated average M–O bond distance difference between Gd^{3+} and Cm^{3+} can be predicted using lanthanide and actinide radii [23]. Bond-valence sum calculations for Cm(1) provide a value of 4.75, which indicates that the bond-valence parameter for it is poorly defined due to insufficient structural data [24,25]. In fact, the recommended bond-valence parameter for Cm^{3+} is 2.23, whereas the parameter for Sm^{3+} is 2.088. These values should be more similar, and the reported value for Cm^{3+} is likely too large. If the Sm^{3+} parameter is used then a reasonable value of 3.24 is obtained for Cm(1). Using the bond lengths found for $Cm(IO_3)_3$, one can calculate that the bond-valence parameter for Cm^{3+} should be approximately 2.06. Clearly, additional single-crystal

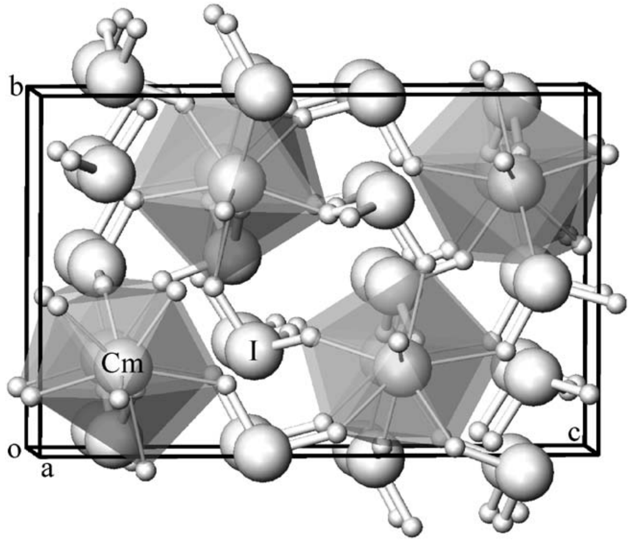

Fig. 2. A view down the *a*-axis of the three-dimensional structure of $Cm(IO_3)_3$.

structural data for curium compounds are needed to validate this value.

There are three crystallographically unique iodate anions in $Cm(IO_3)_3$. The iodate anions containing I(2) and I(3) bridge three Cm^{3+} cations, whereas the iodate containing I(1) bridges two Cm^{3+} cations and has a terminal O(1) oxygen atom. This situation results in the formation of the three-dimensional structure shown in Fig. 2. The I–O bond distances range from 1.784(4) to 1.823(4) Å. In some cases, terminal versus bridging I–O bond distances can be distinguished from one another [2,3], but in this compound this is not the case. In addition to the three short I–O distances around each iodine, there are additional I···O contacts from neighboring iodate anions. I(1) exhibits seven-fold coordination forming a polyhedron that can best be described as a monocapped trigonal prism as a result of three short I–O bonds with distances ranging from 1.795(4) to 1.809(4) Å, two intermediate I–O distances of 3.021(4) and 3.041(4) Å, and two long I–O contacts of 3.292(4) and 3.305(4) Å. The iodate anions containing I(2) and I(3) have three long contacts ranging from 2.709(4) to 2.975(4) Å and 2.788(4) to 3.061(4) Å, respectively, in addition to the three oxygen atoms found in the inner shell of each iodine atom. The six-coordinate polyhedra that result for I(2) and I(3) are highly distorted. Similar bonding arrangements are common in uranyl iodates [2,26,27], and in iodates in general [7,28,29]. Bond-valence sum calculations on I(1), I(2), and I(3) (neglecting the long contacts) yield values of 5.12, 5.17, and 5.08, and are consistent with the presence of I(V) [24,25]. Selected bond distances are given in Table 3.

Table 3
Selected bond distances (Å) and angles (deg) for $Cm(IO_3)_3$

Bond distances			
Cm(1)–O(2)	2.346(4)	I(1)–O(1) (terminal)	1.795(4)
Cm(1)–O(3)	2.505(4)	I(1)–O(2)	1.809(4)
Cm(1)–O(4)	2.315(4)	I(1)–O(3)	1.803(4)
Cm(1)–O(5)	2.479(4)	I(2)–O(4)	1.784(4)
Cm(1)–O(6)	2.403(4)	I(2)–O(5)	1.810(4)
Cm(1)–O(7)	2.458(4)	I(2)–O(6)	1.803(4)
Cm(1)–O(8)	2.568(4)	I(3)–O(7)	1.823(4)
Cm(1)–O(9)	2.375(4)	I(3)–O(8)	1.801(4)
		I(3)–O(9)	1.792(4)
Angles			
O(1)–I(1)–O(2)	100.5(2)	O(5)–I(2)–O(6)	98.7(2)
O(1)–I(1)–O(3)	100.9(2)	O(7)–I(3)–O(8)	102.9(2)
O(2)–I(1)–O(3)	97.5(2)	O(7)–I(3)–O(9)	97.1(2)
O(4)–I(2)–O(5)	96.7(2)	O(8)–I(3)–O(9)	97.0(2)
O(4)–I(2)–O(6)	96.5(2)		

3.2. Raman spectroscopy

Raman spectra have been reported previously for a number of polycrystalline iodates [3,30–34]. Although the isolated IO_3^- has a C_{3v} ($3m$) point group, the site symmetry in crystalline solids is usually reduced to C_{2v}, C_s, or C_1, and as a consequence the Raman profiles are changed. Cumulated data indicate that iodate salts with low IO_3^- site symmetry ($<C_{3v}$) display a strong symmetric I–O stretching mode (ν_1) and two asymmetric modes ν_{3a} and ν_{3b} [35].

All of the atoms in the unit cell of $Cm(IO_3)_3$, found in the C_{2h}^5 space group, occupy 4*e* Wyckoff sites, which are general positions containing C_1 site symmetry. Hence, when compared with the pyramidal C_{3v} ($3m$) symmetry of an isolated IO_3^- ion, the three crystallographically distinct iodate ions have a lower C_1 site symmetry. The 52 atoms in the unit cell consist of a total of 156 fundamental modes represented as $39A_g + 39B_g + 39A_u + 39B_u$. Three of these modes ($A_u + 2B_u$) are acoustic, and are involved in propagation of sound waves in the crystal. The remaining 153 contribute to the normal modes of allowable vibrations. Site group analysis conducted on the crystal indicates that the three distinct iodate anions have internal vibrational contributions of

$$\Gamma_{\text{internal iodate modes}} = 18A_g + 18B_g + 18A_u + 18B_u,$$

where only the A_g and B_g modes are Raman active.

The Raman spectrum of the $Cm(IO_3)_3$ crystal covering the ν_{IO} stretching region is shown in Fig. 3. Of the 36 Raman active modes, 18 are unit cell stretching bands and only a few of these are observed, which include three strong bands with comparable intensities at 760, 804, and 846 cm^{-1}. Weaker bands are also evident at the low- and high-energy sides of the 760 cm^{-1} band with similar weak shoulders at 820 and 859 cm^{-1}.

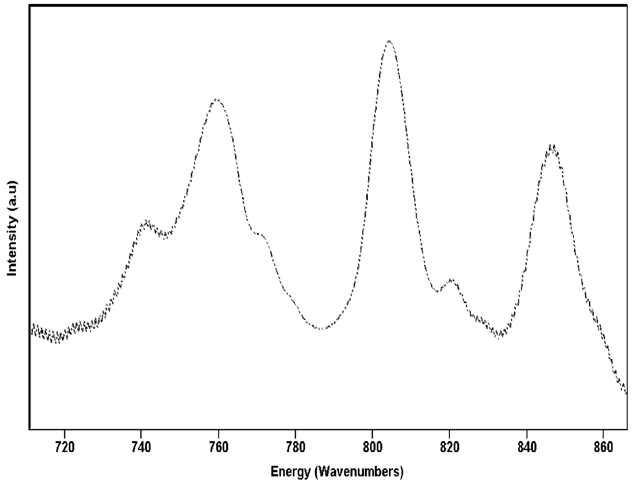

Fig. 3. Raman spectrum of $Cm(IO_3)_3$ shown for I–O stretching modes.

The presence of three crystallographically independent iodate ions complicates the interpretation of the I–O stretching modes. In previous studies of iodate salts of mono- and di-valent cations, criteria for Raman band assignments included comparison of relative intensities, energy positions, and I–O bond strength [30–34]. An intensity comparison can help to differentiate between symmetric stretching and asymmetric modes, as the former usually displays a more intense band than the asymmetric component. In addition, the asymmetric stretching frequency usually shifts to lower energy whenever there is intra-ionic coupling of the three I–O arms of the IO_3^- unit. In contrast, systems where one of the I–O bond distances is significantly shorter than the other two display uncoupled symmetric stretching, and the degeneracy of the asymmetric stretch is lifted. One of the asymmetric components is observed at a higher frequency when compared with the symmetric mode [33,35,36]. Hence, the position of the most intense Raman band, and splitting in the asymmetric mode can be used to ascertain whether coupling between the various I–O modes exists. The orientation of the single crystal may also influence the intensity of the Raman bands.

As shown in Fig. 3, $Cm(IO_3)_3$ has three strong Raman bands with comparable intensities at 760, 804, and 846 cm^{-1}. Assuming negligible inter-ionic coupling, the three bands are assignable to symmetric stretching modes associated with each of the unique iodate ions. Each of the major bands consists of minor components and/or shoulders that correspond to asymmetric contributions. For example, the asymmetric components associated with the 760 cm^{-1} band are observed at 740 and 772 cm^{-1}. Other minor asymmetric components are also observed at 723, 821, 829, and 860 cm^{-1}, providing a total of nine Raman bands in the symmetric stretching region.

A unique feature that is evident in Fig. 3 is the observance of a strong band at a relatively high frequency of 846 cm^{-1}. The appearance of this band for $Cm(IO_3)_3$ was intriguing, since the average I–O stretching frequency reported for iodate salts of mono- and di-valent cations is $\sim$770 cm^{-1} [30,37], and the strongest symmetric stretching band for actinyl iodates is located at $\sim$785 cm^{-1} [3]. Hence, we collected Raman spectra of other trivalent lanthanide and actinide iodates for comparison with the spectrum of $Cm(IO_3)_3$. The high frequency I–O stretching mode for trivalent neodymium and americium salts appears in a similar energy region ($>$840 cm^{-1}), indicating that the *f*-element cations induce a significant shift to the I–O stretching mode [38]. Close inspection of the crystal structure reveals that the I(2) site consists of several distinct features as compared to the other two I(1) and I(3) sites. On average, the I–O distances are not distinguishable with values of 1.802(4), 1.799(4), and 1.805(4) Å for the I(1), I(2), and I(3) sites, respectively. As shown in Table 2, the shortest I–O distance (1.784(4) Å) corresponds to the I(2)–O(4) bond at this site. By inference the I–O bond strength at the I(2) site should be stronger. Another unique feature of this site is that the O–I–O angle, on average, is smaller than the other two sites. The values are 99.6(2)°, 97.3(2)°, and 99.0(2)° for the I(1), I(2), and I(3) sites, respectively. As suggested previously [33] the smaller O–I–O angle at this site induces a higher frequency shift to the I–O symmetric stretching mode. Hence, it is reasonable to assign the high-frequency band to this site.

The cation interaction with the oxygen atoms at the different iodate sites is used to glean the influence of the actinide ion on the frequency of the I–O vibrational profile. The Cm–O distance at the I(2) site is, on average, shorter by $\sim$0.03 and 0.07 Å as compared to the I(1) and I(3) sites, respectively. It is, thus, reasonable to assume that more electron density is withdrawn from the iodate unit at this site. A consequence of such an effect is the strengthening of the I–O bond, which is consistent with the assignment of the highest I–O vibrational band (at 846 cm^{-1}) to the I(2) site.

3.3. Effects of self-irradiation

Usually the color of Cm(III) compounds is light green and the orange/brown color of the $^{248}Cm(IO_3)_3$ single crystals was unexpected. This finding prompted examining the crystal with time, with the expectation that self-irradiation may cause a change. The freshly prepared crystals were observed with time to change first to a dark purple and then to black. However, the crystals continued to diffract well despite this color change, and complete single-crystal X-ray diffraction data collections on the same single crystal revealed virtually no change in the structure over the course of

Table 4
Radiation-induced lattice expansion of $Cm(IO_3)_3$

Data collection	a (Å)	b (Å)	c (Å)	β (°)	V (Å^3)
#1 (17 days)	7.2014(7)	8.5062(9)	13.462(1)	100.142(2)	811.76(14)
#2 (23 days)	7.2117(6)	8.5203(7)	13.485(1)	100.126(2)	815.7(2)
#3 (37 days)	7.2121(7)	8.5235(8)	13.491(1)	100.092(2)	816.5(2)
#4 (71 days)	7.2132(7)	8.5310(8)	13.505(1)	100.021(2)	818.3(2)

seventy-one days or the ability to refine the structure from these data sets. There was a slight increase in the lengths of the unit cell axes and a decrease in the β angle with time, as shown in Table 4. There is not a significant increase in the displacement parameters for the atoms in the crystal structure over the period of time studied. The self-irradiation-induced cell expansion may be caused by alpha-decay events, neutrons or recoiling fission fragments caused from the spontaneous fission of the ^{248}Cm nuclei, or a combination of these. It should also be noted that the 3% ^{246}Cm ($t_{1/2} = 4.76 \times 10^3$ yr, 5.39 MeV alpha) present significantly increases the specific alpha activity of the material and provides more energetic α-particles.

In $^{244}CmO_2$, where radiation damage results in a lattice expansion of approximately 0.25% in a single day [19], reduction of Cm^{4+} to Cm^{3+} is the most significant factor leading to changes in the cell constants [16]. While reduction of Cm^{3+} in $^{248}Cm(IO_3)_3$ is extremely unlikely, a more probable reaction is the partial reduction of IO_3^- to I_2 by radiation, which would account for the color change in this material, although we cannot rule out the formation of color centers caused by the self-irradiation events in the crystals. The former supposition is buttressed by the observation that $UO_2(IO_3)_2(H_2O)$ decomposes by releasing elemental iodine under neutron irradiation [39]. We believe that the color change observed in $Cm(IO_3)_3$ could reflect the formation of small amounts of iodine, and the swelling of the lattice parameters may be a combination of the incorporation of the generated iodine, as well as the effects of α-radiation and neutron emission.

4. Conclusion

In this study we have demonstrated that the type I anhydrous $Ln(IO_3)_3$ (Ln = Ce–Nd, Sm–Lu, and Y) series can be extended to include the transplutonium element, curium. We have shown that the Cm–O bond-valence parameter previously reported for Cm(III) is inaccurate and that additional structural data for compounds containing curium is necessary to establish this value with confidence. Using single-crystal Raman spectroscopy, we have assigned the symmetric and asymmetric modes of the iodate anions in $Cm(IO_3)_3$, and have compared them with values reported for other actinide iodates. Finally, we have shown that even with the use of the longer-lived ^{248}Cm isotope, radiation damage still occurs in crystals of $Cm(IO_3)_3$. The latter is reflected by a small expansion in the lattice parameters by approximately 1% over the course of seventy-one days. This study represents our first report in a series on the systematic study of transplutonium iodates; we plan to extend this series through Cf.

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