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Hydrothermal conversion of cerium oxalate to CeO₂: a parade of oxalate and water coordination modes†

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Hydrothermal conversion of lanthanide/actinide oxalate salts to nanocrystalline oxide has gained technological importance in the chemistry of f-elements. Herein, we present a study describing the mechanism behind the hydrothermal recrystallization and decomposition of cerium (and Ce-Gd) oxalate to oxide. Structural determination of all intermediate nanocrystalline products was possible thanks to three-dimensional electron diffraction. This work reveals the enormous structural abilities of simple oxalate ligands.

Oxalates are low-cost, simple, but essential species in the chemistry of transition metals, lanthanides,¹ and actinides.² Thanks to the low solubility of oxalate salts, oxalic acid is used: as a separation agent of metal ions from aqueous solutions; as a ligand in coordination compounds; in metal-organic frameworks. These salts can be converted readily to nano- and microcrystalline oxides by an appropriate calcination cycle, typically beyond 600 °C.^{3,4} Recently, Walter *et al.*⁵ reported the conversion of uranium(IV) oxalates to oxide under hydrothermal conditions at mild temperatures (160–250 °C). The authors extended their work on the hydrothermal decomposition of various actinide oxalates (Th, U, Np, Pu)⁶ and their solid solutions.^{7,8} Typically, an oxalate dispersion in pure water (pH adjusted or in the presence of hydrazine) is loaded into an autoclave and treated at 100–250 °C. This procedure results in

agglomerates of AnO₂ nanoparticles of approximate size 3 to 10 nm. Later, comprehensive studies were conducted by Manaud *et al.* on Th(IV)⁹ and U(IV)¹⁰ while changing the main reaction parameters (pH, temperature, and time). There was a clear link between the treatment temperature, pH of the solution, and the crystallite size and morphology of the final product. Recently, Baumann *et al.*¹¹ compared the hydrothermal and thermal conversion of Pu(IV) oxalate to nanocrystalline PuO₂ mentioning most of the positive aspects of the hydrothermal route: lower temperature, shorter reaction time, and lower content of residual carbon. All the above-mentioned works described a drastic change in the morphology of the starting powder during the process. However, tracking of the reaction mechanism is complicated due to the hydrothermal conditions, so determination of the structure of intermediates is complicated due to nanocrystallinity. Therefore, the detailed reaction mechanisms are not known. Few studies have described the hydrothermal treatment of cerium oxalate. Flower-like CeO₂ microcrystals were hydrothermally synthesized from an oxalate precursor in an alkaline environment and hydrogen peroxide.¹¹ A similar procedure yielding hierarchical mesoporous ceria was obtained in the presence of some amino acids previously.¹² Recently, mixed U_{1-x}Ce_xO_{2+δ}·nH₂O (0.1 ≤ x ≤ 0.7) solid solutions were prepared using this method.¹³

Herein, we focused on the hydrothermal conversion of pure cerium oxalate hydrate to oxide. Ceria has been in the spotlight for many decades, mainly due to its applicability in fuel cells,¹⁴ catalysis,¹⁵ and Pu surrogates.¹⁶ The mechanism of the decomposition and recrystallisation of oxalate (which is responsible for such a drastic change in the morphology of the agglomerates) was studied in detail. This was possible thanks to the newly developed technique of three-dimensional electron diffraction (3D ED), which enabled complete determination of the structure without the need for large crystals.^{17–22} In addition, we tested the ability of this route to convert mixed Ce_{1-x}Gd_x(C₂O₄)₃·10H₂O solid solutions to Ce_{1-x}Gd_xO_{2-x/2} (x = 0.1, 0.2, 0.3).

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Pure and mixed oxalates were prepared by heterogeneous precipitation as detailed previously^{1,2,3} (a description is in the ESI†). Briefly, for the hydrothermal conversion, 250 mg (0.35 mmol) of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ or $\text{Ce}_{1-x}\text{Gd}_x(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ($x = 0.1, 0.2, 0.3$) was placed in a Teflon™-lined autoclave (capacity of 50 mL) together with distilled water (21 mL) or nitric acid solution of the desired pH. Solutions of HClO_4 and HCl , as nonoxidizing acids, were also tested instead of HNO_3 . The mixture was treated at 180–220 °C for ≥ 24 h. The final product was purified by repeated centrifugation and dried at 50 °C under air. All prepared materials were analysed by powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and thermogravimetric analysis (TGA). The sample was treated in pure water (pH = 7, 220 °C, 48 h) and analysed using 3D ED. A detailed description of the analytical techniques is given in the ESI†.

$\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ can be converted completely to oxide in aqueous nitric acid solution (pH = 1) at >180 °C. Optimal conditions were found to be 24 h and 220 °C to yield a powder of grain size 200–500 nm (Fig. 1). The final size of CeO_2 crystals increased with the applied temperature (see the micrographs in Fig. S1 and infrared spectra in Fig. S2, ESI†).

A short study of the hydrothermal conversion of $\text{Ce}_{1-x}\text{Gd}_x(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ ($x = 0.1, 0.2, 0.3$) solid solutions showed that the conditions mentioned above (HNO_3 solution, pH = 1) were valid for mixed oxides giving homogeneous nanocrystalline $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ (see Fig. S3 and S4 and PXRD in Fig. S5, ESI†). However, the yield of Gd(III) incorporation in CeO_2 was not quantitative and showed some fluctuations (see ICP-MS analyses in Table S1, ESI†). Further studies in this direction are beyond the scope of the current work.

The presence of an oxidizing acid (HNO_3) solution was of paramount importance. It facilitated the oxidation of Ce(III) ions to Ce(IV) ions, leading to the oxide. Hydrothermal

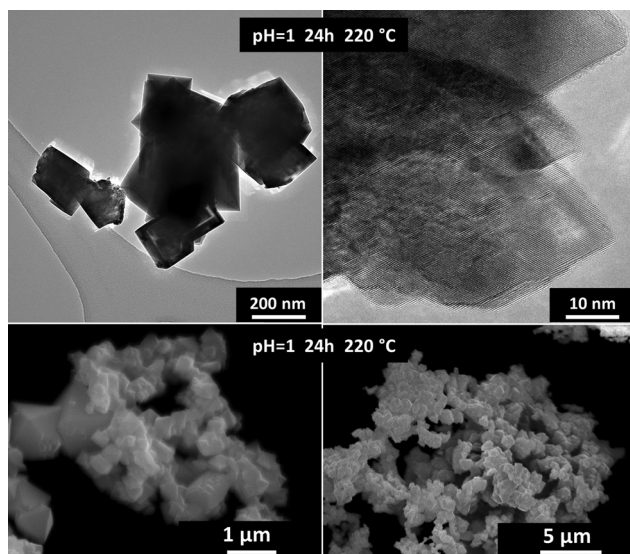


Fig. 1 Transmission (top) and scanning (bottom) electron micrographs of CeO_2 powder obtained by the hydrothermal decomposition of $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ in nitric acid solution (pH = 1) at 220 °C for 24 h.

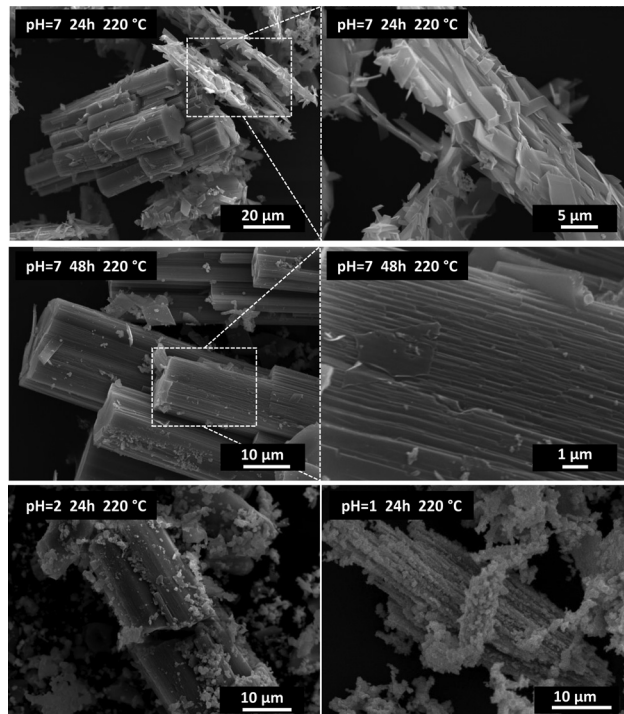


Fig. 2 Scanning electron micrographs of cerium oxalate with different degrees of conversion to CeO_2 . Assemblies of the recrystallised phase with initial $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (top), recrystallisation and change of morphology to rods (middle), and disintegration of the rods to nanocrystalline CeO_2 (bottom).

conversion in HCl or HClO_4 (non-oxidizing acids) solutions of pH = 1 did not lead to CeO_2 (see the XRD results of samples obtained after 24 h at 220 °C in Fig. S6, ESI†). Different concentrations of nitric acid (pH = 1 to 7) in the autoclave batch led to different degrees of conversion. Fig. 2 shows $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ treated in solutions of pH 1 to 7 (HNO_3). In pure water (pH = 7), recrystallisation and a drastic change in morphology occurred, but decomposition to CeO_2 was not reached (Fig. 2, top and middle row). The original cerium oxalate with a flat needle morphology (Fig. S6, ESI†) changed to large rods (from $10 \times 10 \times 100$ µm and larger) with well-developed crystal facets parallel to the elongation direction. Increasing the concentration of nitric acid led to the decomposition of the recrystallized material to oxide (Fig. 2, bottom row). This process was accompanied by full disintegration of the rods to nanocrystals, which sometimes remained assembled to the initial rod shape. A change in agglomerate morphology has been described for all hydrothermally converted oxalates.^{5–10} This is one of the main differences with thermal conversion, during which the initial oxalate shape is retained.^{1,3,23,24}

Recrystallisation was also studied from the crystallographic viewpoint. The PXRD patterns of selected samples were plotted (Fig. 3). Unfortunately, structure matching from PXRD was possible only for the initial cerium oxalate and final cerium dioxide. Tracking the intermediate phases and resolving their structures was difficult due to the nanocrystallinity of the material and the coexistence of several phases in the samples.



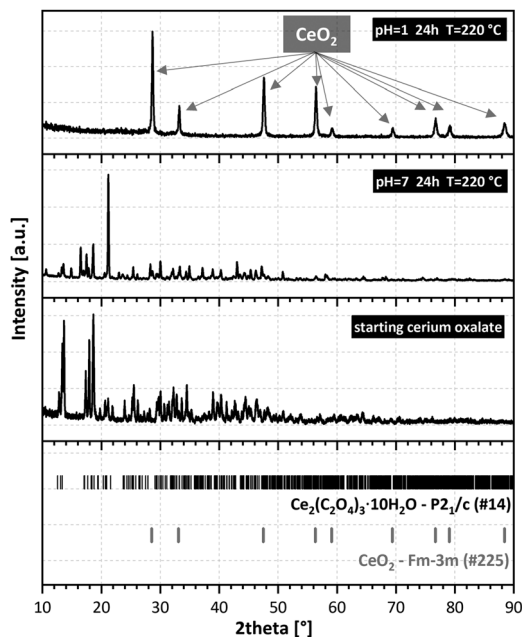


Fig. 3 Powder X-ray diffraction of the initial $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (bottom), hydrothermally treated (middle), and final CeO_2 (top).

This was overcome thanks to 3D ED enabling structural determination of small, unstable, or problematic crystals unsuitable for single-crystal XRD. The structure of the initial oxalate is well known. It crystallizes in the $P2_1/c$ space group with four Ce(III) ions in the elementary cell, each bonded to three oxalate groups and three water molecules in the primary coordination sphere.²⁵ Two additional water molecules are present in each of the four cavities formed by the oxalate coordination polymer. Therefore, the molecular formula should be written as $\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$, as for some An(III) oxalates with a similar structure.²⁶ There are two formula units within the elementary cell. The recrystallized sample at 220 °C (pH = 7, 24 and 48 h) was selected for structural analysis by 3D ED. This sample showed full recrystallization of the oxalate but low decomposition to oxide (Fig. 3). In total, 114 datasets were indexed. Except for the known initial decahydrate structure (42 indexed datasets), four other structures were observed (72 indexed datasets in total), as shown in Table 1 (full information is given in Table S2, ESI†). The structures were all solved *ab initio* by the Superflip program.²⁷ The structure present in most of the transformed oxalate hydrates was the orthorhombic $P2_12_12_1$ of $\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4$. Isostructural Pr and Nd oxalates have been described in the ICSD database.^{28,29} The other three structures have not been reported.

The second most abundant phase was a structure with triclinic $P\bar{1}$ symmetry. If all the water molecules were fully occupied, then the structure was pentahydrate $\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$ (see the detailed discussion of the level of hydration in the ESI†). Four water molecules in the formula unit were coordinated to cerium ions and the fifth one resided in a pore. Two other phases, orthorhombic $Pbcn$ and monoclinic $P2_1/n$, were significantly less abundant and much more disordered judging from the observed diffuse scattering. Both phases were pentahydrate, with four water molecules coordinated to two independent cerium atoms. The fifth water molecule was in a cavity. Hydrolysis or formation of hydroxo-complexes were not observed until the final oxalate decomposition. Probably a higher pH would be required to observe such behavior, as has been observed with Nd.³⁰ The results of 3D ED were supported by PXRD Rietveld analysis of the sample treated at 220 °C for 48 h (Fig. S7, ESI†). The best fit was obtained using the $P2_12_12_1$ and $P\bar{1}$ phases having the highest abundance in the sample.

Evidently, the four structures had common structural motives worth mentioning. In all structures, oxalate ions adopted bridging coordination modes (Fig. S8, ESI†) to connect cerium ions with coordination modes 1:2, 1:2 + 1 and 1:2 + 2 (Fig. S8, top from left, ESI†), extending the list of oxalate coordination modes for rare-earth ions.³¹ The oxalates in the $P2_12_12_1$ structure formed infinite chains along two nearly perpendicular directions, which created a “wine rack” structural motif (Fig. 4, left). Higher coordination numbers in the $Pbcn$, $P\bar{1}$ and $P2_1/n$ structures were probably caused by a specific organization of the infinite chains of oxalates with the 1:2 coordination mode solely, all aligned in the same direction. Layers of oxalates with higher denticity were then perpendicular to these polymer chains (Fig. 4, right), here 1:2 and 1:2 + 2 modes were present.

Six cerium coordination polyhedra were found in the four structures. Type 1 comprised the cerium ion coordinated by nine ligands. Two water molecules were in the *cis* conformation, with one monodentate oxalate and three bidentate oxalates (Fig. S9, ESI†). Types 2, 3, and 4 are shown in Fig. S10 (ESI†). Coordination was achieved by 10 ligands, two water molecules in *trans* positions, and two oxalates in the perpendicular direction forming infinite chains. There were two bidentate oxalates in the other perpendicular direction. Type 5 revealed sole coordination by five oxalates (nine oxalate oxygens (Fig. S11, ESI†)), four bidentates and one monodentate. Type 6 involved non-participation in the infinite chains and, except for three bidentate oxalates, it was coordinated to four water molecules (Fig. S12, ESI†). For more details, see the ESI.†

Table 1 Crystallographic details of hydrothermally recrystallized cerium oxalate phases

Stoichiometric formula	$\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4$	$\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$	$\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$	$\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot \text{H}_2\text{O}$
Occurrence (% of cases)	40	39	14	7
Crystal system	Orthorhombic	Triclinic	Orthorhombic	Monoclinic
Space group	$P2_12_12_1$	$P\bar{1}$	$Pbcn$	$P2_1/n$
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.64(1), 9.59(1), 16.87(1)	10.50(1), 11.77(1), 12.97(1)	22.06(8), 12.96(1), 10.61(1)	21.67(1), 10.51(1), 12.97(1)
α , β , γ (°)	90, 90, 90	92.91(4), 90.58(4), 112.95(4)	90, 90, 90	90, 93.58(4), 90
Z	4	4	8	8



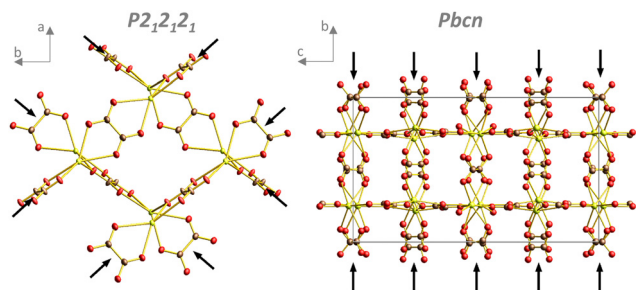


Fig. 4 Oxalates in the $P2_12_12_1$ structure form infinite chains running along two nearly perpendicular directions (black arrows; the other oxalate molecule and coordinated water molecules have been omitted for clarity). $Pbcn$ structure with infinite oxalate chains running only along one direction marked by black arrows (coordinated water molecules and water in pores have been omitted for clarity).

As mentioned above, in the $Pbcn$, $P2_1/n$, and $P\bar{1}$ structures, there were oxalate layers perpendicular to the direction of the infinite oxalate chains. The structural motifs in these layers were almost identical for $Pbcn$ and $P2_1/n$ phases (Fig. 5, left and middle). The difference was that four water molecules were in the layer in the $Pbcn$ structure, but an oxalate replaced it in the $P2_1/n$ phase. The four coordinated molecules in $Pbcn$ pointed outwards from the layer in the direction of the infinite oxalate chains and were coordinated to one cerium atom (type 4). In the $P\bar{1}$ structure, the layer motif was slightly simpler (Fig. 5, right).

The global water content in the sample treated at 220 °C for 24 h was measured by thermogravimetry, and $Ce_2(C_2O_4)_3 \cdot 3.5H_2O$ is shown in Fig. S13 (ESI[†]). From the crystallographic analysis considering two main phases, the composition was estimated to be $Ce_2(C_2O_4)_3 \cdot 4.5H_2O$ (i.e., one water molecule more than determined by thermogravimetry). This was probably caused by lower occupancy of water molecules coordinated to cerium (type 4) and those within the pores (deeper discussion is provided in the ESI[†]).

Similar to that in,^{32,33} hydrothermal crystallization was typically not a single-step process. Here, we reported the mechanism of hydrothermal conversion of $Ce_2(C_2O_4)_3 \cdot 10H_2O$ to oxide. The whole mechanism is expressed graphically in Fig. 6.

Hydrothermal dehydration and recrystallisation of oxalate take place prior to the conversion to oxide, which is responsible for the enormous change in morphology during this process. 3D ED was crucial for structural determination of nanocrystalline samples. The loss of water was linked with an increase in

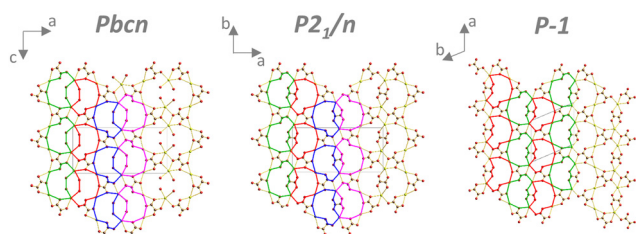


Fig. 5 Structural motifs of oxalate layers perpendicular to the infinite coordination polymer chains. Coordinated water molecules (except those forming the oxalate layer and water in pores) have been omitted for clarity.

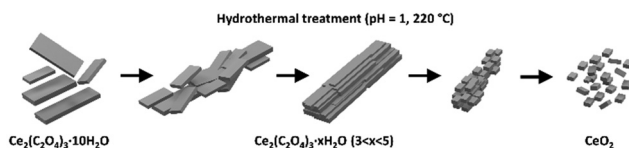


Fig. 6 Graphical illustration of the mechanism of hydrothermal conversion of $Ce_2(C_2O_4)_3 \cdot 10H_2O$ to CeO_2 .

the denticity and coordination mode of the oxalate ligand, and elicited several structurally analogous phases. The change in the oxidation state of cerium, together with oxalate decomposition, seemed to be the final one-step process visible as a disintegration of the recrystallised phases to oxide. In addition to structural investigations, we tested the possibility of hydrothermal conversion of Ce-Gd oxalates to mixed oxides.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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