Supplementary Online Information

Multicomponent Equiatomic Rare Earth Oxides

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Figure S1. XRD patterns of Ce-oxide (a) and Pr-oxides (b) synthesized using the NSP method. The XRD pattern of Ce-oxide matches to CeO\textsubscript{2}. In case of Pr-oxide, lattice parameters as well as refined composition (c) are in agreement with the formation of a compound with composition close to Pr\textsubscript{6}O\textsubscript{11} (PrO\textsubscript{~1.83}), which is known to be the most stable composition for praseodymium oxides at ambient oxygen partial pressures \cite{1}. It is also well known \cite{1} that a composition PrO\textsubscript{2-δ} (δ ≈ 0) can be obtained only at high oxygen partial pressure (280 bar) and low temperature (400 °C). Since the Pr-oxide in this work is synthesized at 1150 °C and 900 mbar in the flowing oxygen atmosphere, presence of only Pr\textsuperscript{4+} is unlikely. In contrast, Pr\textsubscript{2}O\textsubscript{3} can only be obtained using highly reductive reaction atmospheres (e.g., H\textsubscript{2} gas) \cite{1}. 
Figure S2. XRD pattern with the Rietveld refinement of 7-component system, (Ce,Gd,La,Nd,Pr,Sm,Y)O after annealing at 1000 °C for 1 hour showing single-phase (Ia-3) structure.

Structural analysis of (Ce,La,Pr,Sm,Y)O calcined at 1000°C/1h with quenching

As described in the manuscript, the pattern can be indexed using a body centered unit cell with $a_{bcc} = 2a_{fcc}$. Fig. S3 shows a symmetry tree which connects all cubic body centered subgroups to the aristotype CaF$_2$ ($Fm\overline{3}m$) of CeO$_2$. Best fits for a selection of structures are shown in Fig. S4. For all the analyses performed no indication of any ordering of the weakest scatterer Y$^{3+}$ on the different cation sites could be found. The determination of substructure of the oxygen ions is difficult using XRD data only, and neutron diffraction as well as synchrotron XRD could give rise to a better understanding in future studies (these measurements will be conducted in the near future). However, the superstructure reflections seem to mainly arise from small shifts of the lanthanides from their ideal sites in addition to small shift of the oxide ions. It is not possible to unambiguously assign a distinct symmetry, and both branches of the symmetry trees (branch (a) leading to the lowest symmetry $I2_13$ as well as branch (b) leading to a symmetry $I2_3$) result in reasonable fits together with plausible structural data (see Tables S1 and S2). Structures with symmetry Ia-3 and $I2_13$ are well known for some lanthanide oxides (the so-called bixbyite type structure found e.g. for Sm$_2$O$_3$) and result from complete vacancy ordering of the oxide ions. As shown for the refined structure in Table S1, this vacancy ordering seems to be destroyed (Ce,La,Pr,Sm,Y)O, being in agreement with the tetravalent oxidation state of Ce and partially Pr. Therefore, isosymmetric behaviour to the bixbyite is in principle prohibited from stoichiometric reasons already. The structural model with space group I-43m, although resulting in a slightly overall worse fit, shows some significant improvement regarding the fit of the superstructure reflections (e.g. the reflection at $2\theta = 54.5^\circ$). Also for this structure type, neither ordering of oxygen vacancies (in agreement with compositional considerations) nor ordering of Y$^{3+}$ is indicated from the refinement, and the structures distinguishes from the bixbyite in terms of slightly different site occupancies of the oxide ions as well as different local site symmetries with a different splitting pattern of the cation sites.
Figure S3. Group–subgroup relationships connecting the fluorite type structure of CeO$_2$ to all potential body centred subgroups. Figures are derived using the tools provided on the Bilbao Crystallographic Server [2–4]. (S1,S2 – Different settings with non-equivalent symmetry exist for this space group; (*) – Different settings exist which are symmetrically equivalent but distinguish by the choice of origin; (#) – Model does not need to be tested since the corresponding subgroup model of $I2\overline{3}$ does not give a proper fit; $R_{wp}$ values are given for Rietveld fits of different structural models. Fits are shown for red values in Fig. S4.
Figure S4. Rietveld fits of different structural models for (Ce,La,Pr,Sm,Y)O (also see Fig. S7). Refined structural data are provided for models with symmetry of $I-43m$ and Ia-3 (see Tables S1 and S2).
Table S1. Structural model for (Ce,La,Pr,Sm,Y)O, space group Ia-3, a = 10.95604(18) Å (five positional parameters are used for the refinement).

| Site | Wyckoff site | x  | y  | z  | Atom type | Occupation | B [Å] |
|------|--------------|----|----|----|-----------|------------|-------|
| Ln1  | 8b           | ¼  | ¼  | ¼  | Ce<sup>4+</sup> | 0.2        | 0.34(3) |
|      |              |    |    |    | La<sup>3+</sup> | 0.2        | 0.34(3) |
|      |              |    |    |    | Pr<sup>3+</sup> | 0.2        | 0.34(3) |
|      |              |    |    |    | Sm<sup>3+</sup> | 0.2        | 0.34(3) |
|      |              |    |    |    | Y<sup>3+</sup>  | 0.2        | 0.34(3) |
| Ln2  | 24d          | 0.01633(18) | 0  | ¼  | Ce<sup>4+</sup> | 0.202(6)   | 0.34(3) |
|      |              |    |    |    | La<sup>3+</sup> | 0.202(6)   | 0.34(3) |
|      |              |    |    |    | Pr<sup>3+</sup> | 0.202(6)   | 0.34(3) |
|      |              |    |    |    | Sm<sup>3+</sup> | 0.202(6)   | 0.34(3) |
|      |              |    |    |    | Y<sup>3+</sup>  | 0.202(6)   | 0.34(3) |
| O1   | 48e          | 0.866(2)  | 0.361(2)  | 0.396(2) | O<sup>2-</sup> | 0.83(2)  | 0.34(3) |
| O2   | 16c          | 0.128(4)  | 0.128(4)  | 0.128(4) | O<sup>2-</sup> | 1.00(3)  | 0.34(3) |

Table S2. Structural model for (Ce,La,Pr,Sm,Y)O, space group I-43m, a = 10.95604(18) Å (eight positional parameters are used for the refinement).

| Site | Wyckoff site | x  | y  | z  | Atom type | Occupation | B [Å] |
|------|--------------|----|----|----|-----------|------------|-------|
| Ln1  | 2a           | 0  | 0  | 0  | Ce<sup>4+</sup> | 0.2        | 0.37(3) |
|      |              |    |    |    | La<sup>3+</sup> | 0.2        | 0.37(3) |
|      |              |    |    |    | Pr<sup>3+</sup> | 0.2        | 0.37(3) |
|      |              |    |    |    | Sm<sup>3+</sup> | 0.2        | 0.37(3) |
|      |              |    |    |    | Y<sup>3+</sup>  | 0.2        | 0.37(3) |
| Ln2  | 6b           | 0  | ½  | ½  | Ce<sup>4+</sup> | 0.198(9)   | 0.37(3) |
|      |              |    |    |    | La<sup>3+</sup> | 0.198(9)   | 0.37(3) |
|      |              |    |    |    | Pr<sup>3+</sup> | 0.198(9)   | 0.37(3) |
|      |              |    |    |    | Sm<sup>3+</sup> | 0.198(9)   | 0.37(3) |
|      |              |    |    |    | Y<sup>3+</sup>  | 0.198(9)   | 0.37(3) |
| Ln3  | 24g          | 0.7540(3) | 0.7540(3) | 0.4847(2) | Ce<sup>4+</sup> | 0.195(7) | 0.37(3) |
|      |              |    |    |    | La<sup>3+</sup> | 0.195(7)   | 0.37(3) |
|      |              |    |    |    | Pr<sup>3+</sup> | 0.195(7)   | 0.37(3) |
|      |              |    |    |    | Sm<sup>3+</sup> | 0.195(7)   | 0.37(3) |
|      |              |    |    |    | Y<sup>3+</sup>  | 0.195(7)   | 0.37(3) |
| O1   | 24g          | 0.890(3)  | 0.890(3)  | 0.353(3) | O<sup>2-</sup> | 0.80(12) | 0.37(3) |
| O2   | 24g          | 0.877(3)  | 0.877(3)  | 0.615(3) | O<sup>2-</sup> | 0.98(12) | 0.37(3) |
| O3   | 8c           | 0.849(2)  | 0.849(2)  | 0.849(2) | O<sup>2-</sup> | 1.00(13) | 0.37(3) |
| O4   | 8c           | 0.149(4)  | 0.149(4)  | 0.149(4) | O<sup>2-</sup> | 0.87(14) | 0.37(3) |

References

[1] Holleman AF, Wiberg EN. Lehrbuch der Anorganischen Chemie (Textbook of Inorganic Chemistry). Berlin; New York: Walter de Gruyter; 1995.
[2] Aroyo MI, Perez-Mato JM, Capillas C, Kroumova E, Ivantchev S, Madariaga G, Kirov A, Wondratschek H. Bilbao Crystallographic Server: I. Databases and crystallographic computing programs. Zeitschrift fur Kristallographie. 2006;221:15–27.
[3] Aroyo MI, Kirov A, Capillas C, Perez-Mato JM, Wondratschek H. Bilbao Crystallographic Server. II. Representations of crystallographic point groups and space groups. Acta Crystallographica Section A Foundations of Crystallography. 2006;62:115–128.
[4] Aroyo MI, Perez-Mato JM, Orobenegou D, Tasci E, De La Flor G, Kirov A. Crystallography online: Bilbao crystallographic server. Bulgarian Chemical Communications. 2011;43:183–197.