Supporting Information

Multicomponent equiatomic rare earth oxides with narrow band gap and associated praseodymium multivalency

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Oxides	<i>f</i> [wt. %]	<i>a</i> [Å]	<i>D</i> [nm]
As-synthesized, $(Fm\bar{3}m)$			
CeO ₂	100	5.4135(1)	15.7(3)
$(Ce,Pr)O_{2-\delta}$	100	5.4392(3)	6.8(1)
(Ce,La,Pr)O _{2-δ}	100	5.5203(2)	10.5(2)
(Ce,La,Pr,Y)O _{2-δ}	100	5.4962(3)	6.8(2)
(Ce,La,Pr,Sm)O _{2-δ}	100	5.5276(3)	7.8(2)
(Ce,La,Pr,Sm,Y)O _{2-δ}	100	5.5071(4)	7.5(2)
(Ce,La,Nd,Pr,Sm,Y)O _{2-δ}	100	5.4998(1)	a
(Ce,Gd,La,Nd,Pr,Sm,Y)O _{2-δ}	97.1	5.5168(4)	a
Calcined, $(Ia\overline{3})$			
(Ce,La,Pr,Sm,Y)O _{2-δ}	100	10.9567(2)	28.8(7)
(Ce,La,Nd,Pr,Sm,Y)O _{2-δ}	100	10.9319(3)	31.0(1)
$(Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta}$	100	10.9625(2)	34.0(2)
$(Ce,La,Nd,Pr,Sm,Y)O_{2-\delta}$ $(Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta}$ $(Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta}$ $(Ce,La,Pr,Sm,Y)O_{2-\delta}$ $(Ce,La,Nd,Pr,Sm,Y)O_{2-\delta}$ $(Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta}$	100 97.1 100 100 100	5.4998(1) 5.5168(4) 10.9567(2) 10.9319(3) 10.9625(2)	$\begin{array}{c} -a \\ -a \\ 28.8(7) \\ 31.0(1) \\ 34.0(2) \end{array}$

Table S1. Summary of results obtained from the Rietveld refinement of as-synthesized ME-REOs: fraction of main phase, i.e., fluorite (*f*), lattice parameter (*a*), and crystallite size (*D*). Oxides $f[wt \%] = a[\AA] = D[nm]$

^amain contribution to peak broadening arises from strain

Oxidation state of Pr and lattice parameter variation with respect to cationic radii. Figure

S1 shows variation of the lattice parameters of the different multicomponent equiatomic rare earth oxides (ME-REOs) with respect to average cationic radii, *r*, which is calculated by taking an average of the ionic radii¹ of all the cations, considering their oxidation (either 3+ or 4+) state and coordination number (8). The values of the average cationic radii of all the ME-REO systems are given in Table S2. The changes in the lattice parameter are often linearly related to the average cationic size (which is dependent on the valence state) in accordance with Vegard's law. The same trend is also observed in ceria based (or related) systems.² Conversely, the average radii of the cations (and hence, their valence state) can also be deduced if the variation of the lattice parameter is known. In order to get a better picture regarding the actual oxidation state of Pr three cases are considered: (a) Pr is considered to be in only 4+ state, (b) Pr is considered to in a mixed 3+/4+ oxidation state with ratio of 3+ to 4+ is same as in Pr_6O_{11} and (c) where Pr is considered to be in only 3+ state. The oxidation state of all the other cations are kept constant, i.e., Ce^{4+} , Gd^{3+} , La^{3+} , Nd^{3+} , Sm^{3+} , Y^{3+} . From the Fig S1 (a) – (c), it can clearly be seen that Vegard's law, i.e., a linear trend is followed only in case (b) where Pr is assumed to be in a mixed oxidation state. This result is in good agreement with the XPS result and hence, it can be stated that Pr is a multivalent state with Pr^{3+} : Pr^{4+} ratio being same as in Pr_6O_{11} , i.e., 1: 2.

Oxides	Average cationic radii, r, [Å]			
	Case (a)	Case (b)	Case (c)	
CeO ₂	0.970	0.970	0.970	
$(Ce,Pr)O_{2-\delta}$	0.965	1.050	0.993	
$(Ce,La,Pr)O_{2-\delta}$	1.019	1.075	1.042	
(Ce,La,Pr,Y)O _{2-δ}	1.042	1.085	1.056	
(Ce,La,Pr,Sm)O _{2-δ}	1.025	1.067	1.037	
(Ce,La,Pr,Sm,Y)O _{2-δ}	1.036	1.070	1.048	
(Ce,La,Nd,Pr,Sm,Y)O _{2-δ}	1.039	1.067	1.043	
$(Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta}$	1.037	1.061	1.055	
$\begin{array}{l} (Ce,La,Pr)O_{2-\delta} \\ (Ce,La,Pr,Y)O_{2-\delta} \\ (Ce,La,Pr,Sm)O_{2-\delta} \\ (Ce,La,Pr,Sm,Y)O_{2-\delta} \\ (Ce,La,Nd,Pr,Sm,Y)O_{2-\delta} \\ (Ce,Gd,La,Nd,Pr,Sm,Y)O_{2-\delta} \end{array}$	1.019 1.042 1.025 1.036 1.039 1.037	1.075 1.085 1.067 1.070 1.067 1.061	1.042 1.056 1.037 1.048 1.043 1.055	

Table S2. Values of the average cationic radii of ME-REOs where in (a) Pr is considered only in 4+ state (b) Pr is in multivalent (3+/4+) state with Pr^{3+} : Pr^{4+} is 1 : 2 (c) Pr is in only 3+ state.



Figure S1. Variation in lattice parameters of different ME-REOs as a function of average cationic radii where Pr is considered to be only in 4+ oxidation state in (a), in a mixed (3+,4+) oxidation state (b) and only in 3+ oxidation state (c).Vegard's law is followed only in case (b).

ME-REOs without Pr. Three ME-REO systems without Pr are synthesized under the same conditions that are used for the synthesis of ME-REOs with Pr. The XRD patterns of these three systems are shown in Figure S2a. Two of the systems (Ce,La,Sm)O_{2.δ} and (Ce,La,Sm,Y)O_{2.δ} crystallize as single phase fluorite type structure with lattice parameters 5.5457(0) Å and 5.5144(0) Å, respectively. In other systems, containing 5 cations (Ce,La,Nd,Sm,Y)O_{2.δ}, a small amount (~ 4.5 wt. %) of secondary La₂O₃ type phase alongside the main fluorite type phase (a = 5.5232(1) Å) is observed. Except for Ce all the RE elements in these three systems are expected to be in 3+ oxidation state justifying the selection of the non-stoichiometric formula. All the systems show strong absorption only below 450 nm and the direct band gap are in the range of 2.91 - 3.04 eV (see Figure S2b). The difference in the band gap between these systems and ceria is around 0.30 - 0.15 eV which can be because of the presence of oxygen vacancies in these systems.



Figure S2. XRD patterns (a) and Tauc plots (b) for ME-REOs without Pr. The XRD pattern confirms the phase purity of the systems while the Tauc plots show that the band gap of these ME-REOs without Pr are in the range of 2.91 - 3.04 eV.

References

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- (2) Omar, S.; Wachsman, E. D.; Nino, J. C. Higher Conductivity Sm3+ and Nd3+ Co-Doped Ceria-Based Electrolyte Materials. *Solid State Ionics* **2008**, *178* (37–38), 1890–1897.