Supplementary information

Determining factor for interstitial oxygen formation in Ruddlesden-Popper type La₂NiO₄-based oxides.

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Table S1. Concentration and malar ratio of cations in La_2NiO_4 , $La_2(Ni_{0.9}Fe_{0.1})O_4$, $La_2(Ni_{0.9}Co_{0.1})O_4$ and $La_2(Ni_{0.9}Cu_{0.1})O_4$ evaluated by ICP-AES.

Concentration (wt%)	La	Ni	Dopant (Fe, Co, Cu)
La ₂ NiO ₄	69.8	14.7	-
$La_2(Ni_{0.9}Fe_{0.1})O_4$	70.2	13.1	1.36
La ₂ (Ni _{0.9} Co _{0.1})O ₄	70.2	13.3	1.44
$La_2(Ni_{0.9}Cu_{0.1})O_4$	70.0	13.1	1.53
Molar ratio	La	Ni	Dopant (Fe, Co, Cu)
La ₂ NiO ₄	2.0	1.0	-
$La_2(Ni_{0.9}Fe_{0.1})O_4$	2.0	0.88	0.10
La ₂ (Ni _{0.9} Co _{0.1})O ₄	2.0	0.90	0.10
La ₂ (Ni _{0.9} Cu _{0.1})O ₄	2.0	0.89	0.11



Figure S1. XRD patterns of La₂NiO₄, La₂(Ni_{0.9}Fe_{0.1})O₄, La₂(Ni_{0.9}Co_{0.1})O₄ and La₂(Ni_{0.9}Cu_{0.1})O₄.



Figure S2. (a) Ni *L*-edge and (b) O *K*-edge spectra of La_2NiO_4 annealed at 1bar O_2 at 1073 K. Red and black lines show XAS spectra obtained by FY method and TEY method, respectively. In both cases, the contribution of La is significantly large in TEY method.



Figure S3. The comparison of FY and TEY spectra of (a) Fe *L*-edge, (b) Co *L*-edge and (c) Cu *L*-edge of reference materials. TEY spectra indicates unexpected surface oxidation of the reference materials. FY spectra are distorted by the effect of self-absorption.



Figure S4. (a) Fe *L*-edge spectra of of $La_2(Ni_{0.9}Fe_{0.1})O_{4+\delta}$ FeO and Fe₂O₃. (b) Co *L*-edge spectra of $La_2(Ni_{0.9}Co_{0.1})O_{4+\delta}$ CoO and LiCoO₂. (c) Cu *L*-edge spectra of $La_2(Ni_{0.9}Cu_{0.1})O_{4+\delta}$ Cu₂O and CuO. Green and blue lines show the XAS spectra of reference materials obtained by FY method.



Figure S5. Ni *L*- and O *K*-edges of B-site doped La_2NiO_4 . Dashed line shows the XAS spectra of the sample pre-annealed in 10⁻⁴ bar at 1073 K.



Figure S6. Calculation of integrated pre-edge peak intensity of O *K*-edge spectra. Auxiliary line 1 is the background and auxiliary line 2 is the extension of the main edge. Shaded area is the integrated pre-edge peak intensity which semi-quantitatively indicate unoccupied pDOS in O2*p* hybridized with transition metal 3*d*.