





FIG.S1 Thermogravimetric analysis (TGA) in air (a) $LaSrCo_{0.5}Ru_{0.5}O_4$, (b) $LaSrNi_{0.5}Ru_{0.5}O_4$ and (c) $LaSrZn_{0.5}Ru_{0.5}O_4$.



FIG.S2 XRD patterns recorded after the TGA measurements. $* = La_{1-x}Sr_xM_{0.5}Ru_{0.5}O_3$ (M = Co, Ni and Zn). $\# = La_2O_3$.











FIG.S3 Comparison of a single Lorentzian line with Two Lorentzian line about Ru 3d spectra.

Table S1

Parameters obtained from deconvolution of XPS core Ru_{3d} spectra using CASA XPS software. The spectrum is normalized based on the Sr $3p_{3/2}$ peak binding energy. $\Delta E_{spin-orbit}$: spin-orbit splitting of the Ru 3d peak.

Compound name	Ru <i>3d</i> _{5/2} B.E.	$\Delta E_{spin-orbit}(eV)$	Ru	Isatellite/	Ru <i>3p</i> _{3/2} B.E.
	(eV)		$\Delta E_{\text{satellite}}$	I _{main}	(eV)
LaSrCo _{0.5} Ru _{0.5} O ₄	282.4	4.3	1.4	0.35	463.8
LaSrNi _{0.5} Ru _{0.5} O ₄	282.3	4.3	1.3	0.40	463.9
$LaSrZn_{0.5}Ru_{0.5}O_4$	282.4-283.4	3.9	1.5	0.40	464.2
SrRuO3	281.4-281.9	4.1			

Not only the absolute energy of Ru $3d_{5/2}(282.3 \text{ Vs } 281.9 \text{eV})$ but also spin-orbit splitting of the Ru 3d peak (4.3 Vs 4.1 eV) suggested the two Lorentzian lines should be adopted. We postulated the equal proportion of the total area in every Ru $3d_{3/2}$ and Ru $3d_{5/2}$ peak and similar FWHM. Therefore constraints have been made by linking relative area and FWHM terms in every Ru 3d peak, and at the same time let position of each peaks move automatically. The fitting of Non-symmetrical Ru 3d spectra was improved. The positions of each peak were consistent with the peaks of Non-symmetrical Ru 3d spectra (please check arrows).

The ruthenates (strongly correlated oxides), is characteristic of itinerant electron behavior. The presence of mixed valency is quite normal .In fact, there are many examples about it. The most famous example is double perovskites Sr_2FeMoO_6 , involving the $Fe^{3+}+Mo^{5+}=Fe^{2+}+Mo^{6+}$ charge transfer[58].

[58] García-Landa B . Ritter C . Ibarra M R . Blasco J . Algarabel P A . Mahendiran R.

García J . [J]. Solid State Commun., 1999,110: 435.