Table S1: Refined structural parameters and selected bond lengths and angles of $LaCu_3Fe_4O_{12}$ from the Rietveld analysis of SXRD data at 100, 300 and 450 K. Space group is $Im\bar{3}$ (Z = 2, No. 204). The atomic positions are 2*a*(0, 0, 0), for La; 6*b*(0, 0.5, 0.5), for Cu; 8*c*(0.25, 0.25, 0.25), for Fe and 24*g*(*x*, *y*, 0), for O. Numbers in parentheses are standard deviations of the last significant digit.

T (K)	100	300	450
a (Å)	7.42455(5)	7.43283(4)	7.41420(6)
V (Å^3)	409.270(8)	410.641(7)	407.561(9)
x (O)	0.3112(4)	0.3111(3)	0.3070(4)
y (O)	0.1705(4)	0.1711(4)	0.1764(4)
U_{iso}(La) (100×Å^2)	0.01(1)	0.26(2)	0.42(2)
U_{iso}(Cu) (100×Å^2)	0.82(2)	1.09(2)	1.48(3)
U_{iso}(Fe) (100×Å^2)	0.07(1)	0.14 (2)	0.22(2)
U_{iso}(O) (100×Å^2)	0.32(7)	0.36(7)	0.67(8)
La-O (Å) (×12)	2.634(3)	2.639(3)	2.625(3)
Cu-O (Å) (×4)	1.889(3)	1.895(2)	1.937(3)
(×4)	2.820(4)	2.819(3)	2.780(3)
(×4)	3.365(5)	3.364(6)	3.326(4)
Fe-O (Å) (×6)	2.0000(10)	2.0007(9)	1.9778(10)
Fe-O-Fe (°)	136.3(2)	136.5(1)	139.2(2)
R_p (%)	5.78	4.70	5.42
R_{wp} (%)	7.40	6.70	7.71

Table S2: Bond valence sum values (V_i) for Cu and Fe sites in $LaCu_3Fe_4O_{12}$ at 100, 300, and 450 K. The V_i is calculated using the formula $V_i = \sum_j S_{ij}$, and $S_{ij} = \exp[(r_0 - r_{ij})/0.37)]$. The following r_0 values were used: 1.739 (ref. 29) and 1.649 (ref. 30) for Cu^{3+} and Cu^{2+}, respectively, with twelve coordinated oxygen atoms; 1.751 (ref. 31) and 1.772 (ref. 32) for Fe^{3+} and $Fe^{3.75+}$, respectively, for six coordinated oxygen atoms. For the $Fe^{3.75+}$ site at 450 K, the r_0 of Fe^{4+} ion was used for the calculation.

T (K)	100	300	450
Cu	2.93	2.90	2.06
Fe	3.06	3.05	3.44

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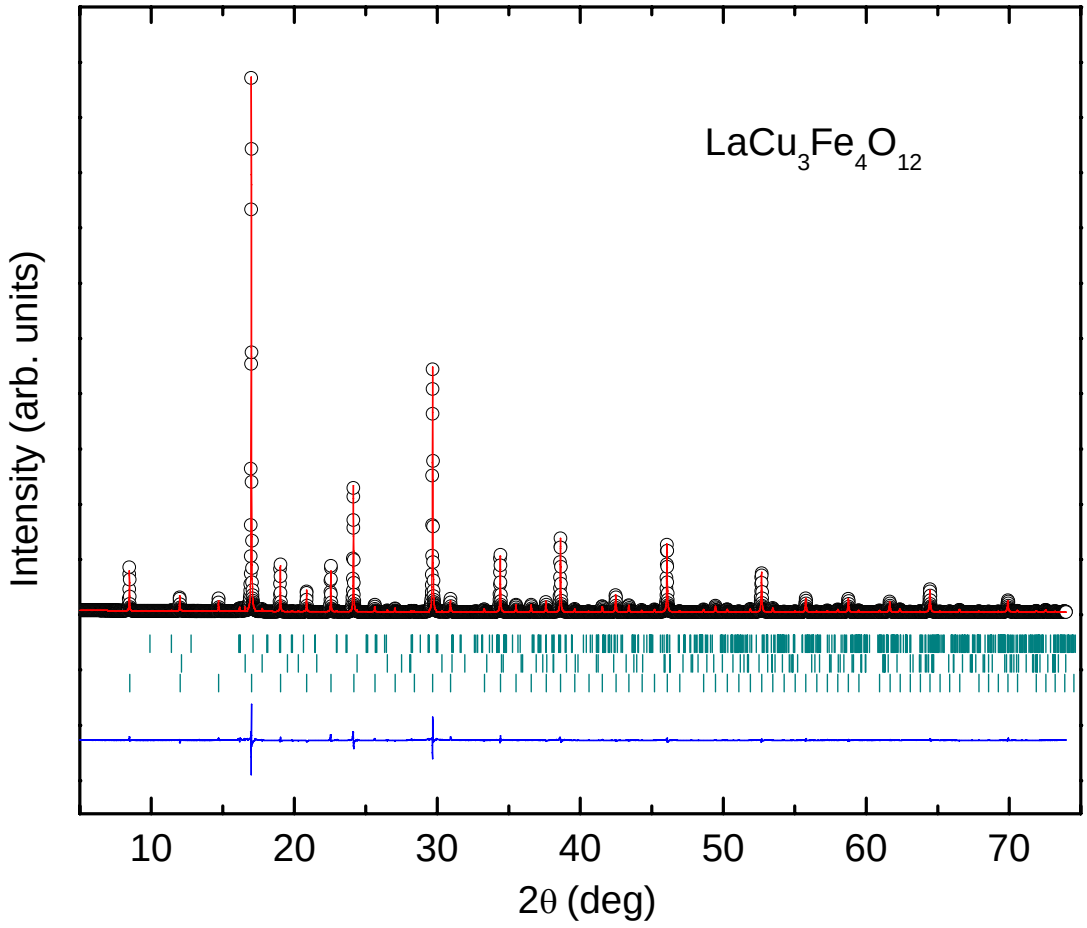

Figure S1: SXRD pattern of $LaCu_3Fe_4O_{12}$ at 300 K and the Rietveld refinement profile. The observed (○), calculated (—), and difference (—) patterns are shown. The bottom-row ticks mark the positions of allowed Bragg reflections of $LaCu_3Fe_4O_{12}$. The sample contains small amount of impurities: 0.4 *wt*% $LaFeO_3$ (top-row ticks) and 1.6 *wt*% α-Fe_2O_3 (middle-row ticks).

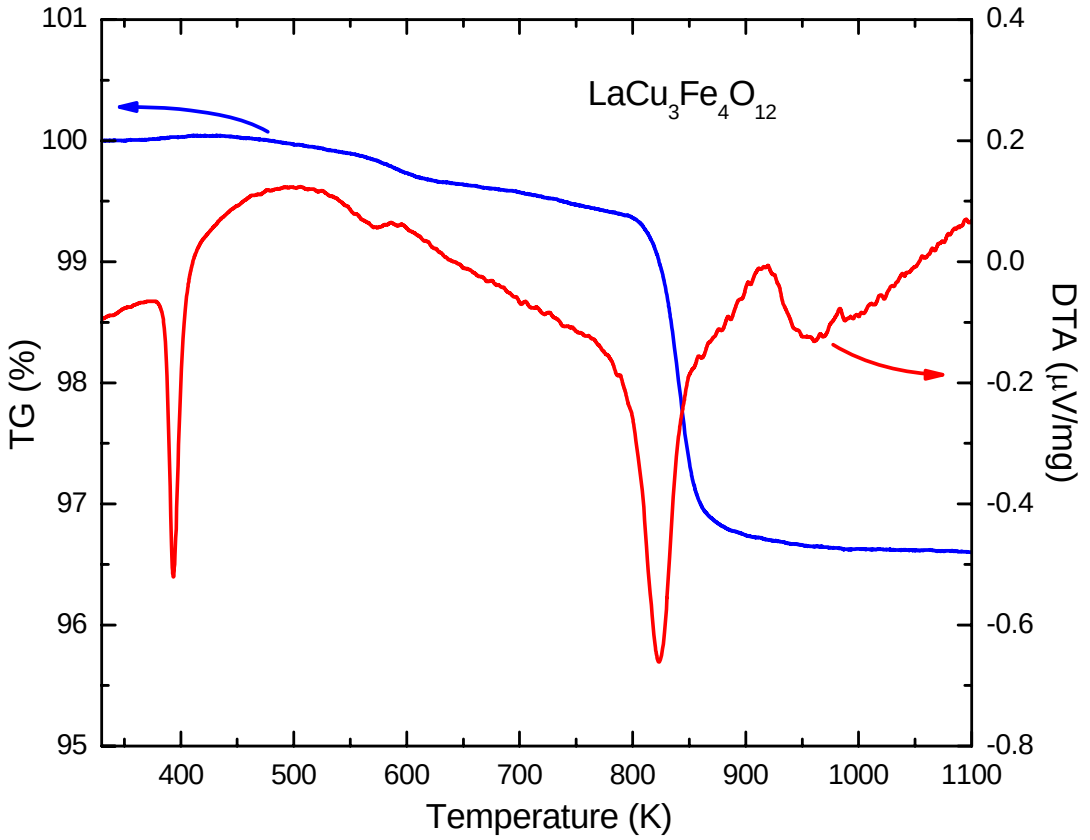

Figure S2: Results of thermogravimetry (TG) and differential thermal analysis (DTA). The sharp peak at 393 K in the DTA curve shows a phase transition, and at temperatures above ~820 K the sample decomposed into $LaFeO_3$, $CuFe_2O_4$ and CuO (identified by X-ray diffraction). The TG loss (~3.25%) is consistent with the amount of released oxygen (3.22%) expected from the reaction $LaCu_3Fe_4O_{12} \rightarrow LaFeO_3 + 3/2CuFe_2O_4 + 3/2CuO + 3/4O_2$, confirming the oxygen stoichiometry of $LaCu_3Fe_4O_{12}$.