Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary Information

Solvothermal and mechanochemical intercalation of Cu into $La_2O_2S_2$ enabled by the redox reactivity of $(S_2)^{2-}$ pairs

Experimental procedures

1. X-ray diffraction

Powder X-ray diffraction (XRD) patterns were recorded at room temperature on a Bruker D8 Advance Diffractometer (Bragg-Brentano geometry, θ-2θ), which employs Cu $K_{\alpha 1}$ radiation (λ = 1.540598 Å) produced through Ge (111) monochromator and LynxEye detector.

2. 3D electron diffraction analyses

The brown powder obtained after solid-solid reaction between 2.0 eq. of Cu and $La_2O_2S_2$ was used for TEM analyses. The powder sample was dispersed in ethanol and a drop of the suspension was deposited and dried on a copper grid with a thin film of holey amorphous carbon. 3D electron diffraction (3D ED) data sets [1,2] were collected with the precession electron diffraction tomography (PEDT) technique [3–6] on a Philips CM120 electron transmission microscope (TEM) (Vacc=120 kV, LaB_6) coupled with the precession device Nanomegas Digistar and a side-mounted CCD camera Olympus Veleta with 14-bit dynamic range. Non-oriented patterns were recorded stepwise at the ambient temperature on 2 nanocrystals (Fig. 3) with ~200 nm diameter. The precession angle was set to 1 degree with a tilt step of 1 degree. A condenser aperture of 10 µm and low illumination setting (spot size 7) were used to preserve the crystal during the data collection. PEDT data were analyzed using the computer programs PETS2.0[7] and JANA2006.[8] For each data set, two lists of *hkl*-indices with associated intensities and estimated standard deviations are obtained: one for the structure solution and another one for the dynamical refinement. We adopted the parameters suggested by Palatinus et al.[9-10] to select reflections involved in the dynamic refinement: *RSg*(max) = 0.65, Sg(max) (matrix) = 0.01 $Å^{-1}$ and *g*(max) = 1.7 $Å^{-1}$.

Results

1. 3D electron diffraction analyses

The analysis of the PEDT data gives a tetragonal unit-cell with $a \approx 4.01(1)$ Å, and $c \approx 8.46(6)$ Å that is consistent with our previous Rietveld refinement for the intercalated phase ($a = 3.9982(5)$ Å and $c = 8.5125(3)$ Å)[13] as well as the powder sample prepared by high-temperature synthesis at $T = 800$ °C ($a = 3.99625(5)$ Å and $c = 8.51743(9)$ Å).[11] The space group *P*4/*nmm* is compatible with the sections of the reciprocal space (Fig. S1). The model was solved in JANA2006 using the charge flipping algorithm in the program Superflip.[12] Two data sets were combined to reach 90% coverage (for $\theta = 1.34$ deg) in the *P*4/*nmm* space group with 119/125 observed over all independent reflections (averaged from the 1625/1792 measured). The refined atomic positions for lanthanum $z/c = 0.1439(3)$ and sulfur $z/c = 0.6729(1)$, which are comparable to our previous refinement based on XRD data ($z/c = 0.1473(2)$ and $z/c = 0.6627(4)$ for lanthanum and sulfur, respectively).

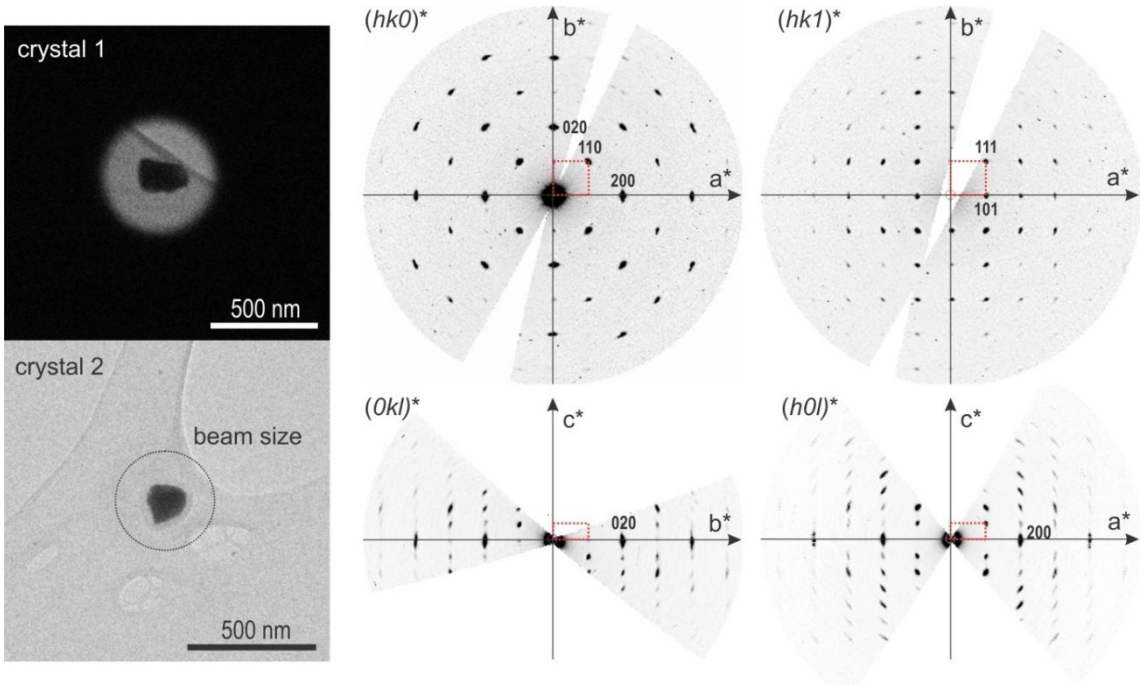

Fig. S1. From the left to the right, picture of the two $La_2O_2Cu_2S_2$ crystals used in the structural characterization and sections of the reciprocal space reconstructed in PETS2.0. The unit-cell is represented in red.

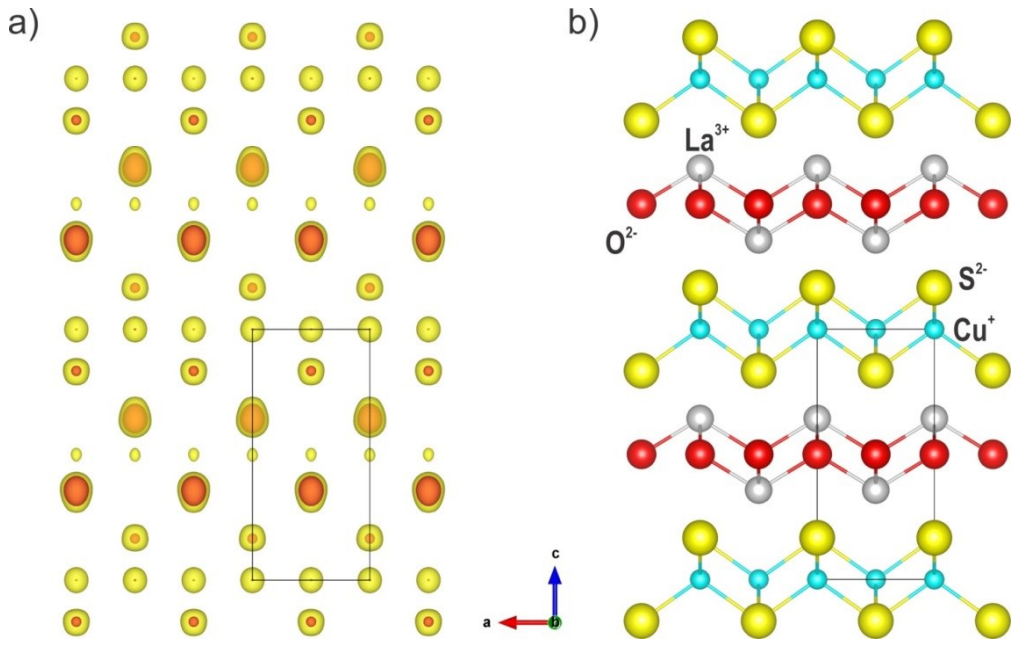

Fig. S2. *(*a) Projection along **b** of the 3D electrostatic potential map (direct solution) and, (b) corresponding model for $La_2O_2Cu_2S_2$.

Table S1. Summary of PEDT data collection conditions and refinement parameters for $La_2O_2Cu_2S_2$.

Structural formula	$La_2O_2Cu_2S_2$
Unit–cell parameters (RXPD)	a = 3.9982(5) Å, c = 8.5125(3) Å
V	136.08(1) Å^3
Z	1
Space group	*P4/nmm*
d_{calc} (g.cm^{-3})	6.1139 (for the formula given above)
Temperature	ambient T
Diffractometer	TEM Philips CM120
Radiation (wavelength)	electrons, (0.0335 Å)
Resolution	0.1–0.7 Å^{-1}
Limiting Miller indices	0≤ h ≤3, 1≤ k ≤5, 0≤ l ≤11
Coverage	90%
No. of independent reflections (obs/all) – kinematic	119/125
R_{int} (obs/all) – kinematic	0.1674/0.2164
Redundancy	12.237
Dynamical refinement by Jana2006:	
Reflection selection parameter	RS_g(max) = 0.65
No. of reflections (obs/all)	2339/2905
R, *wR (obs)*	0.1261/0.1451
N parameters/*N* struct. parameters	201/6

Table S2. Atom positions, displacement parameters (equivalent/isotropic, in Å^2) for the crystal structure of $La_2O_2Cu_2S_2$.

Atom	*Wyck.*	*x*/*a*	*y*/*b*	*z*/*c*	*Occ.*	U_{iso} (Å^2)
La1	2c	0	0.5	0.1439(3)	1	0.0100(5)
Cu1	2b	0	0	0.5	1	0.0332(10)
S1	2c	0	0.5	0.6729(11)	1	0.0274(11)
O1	2a	0	0	0	1	0.0043(13)
distances	Cu1-S1:	2.482(6) Å,	La1-O1:	2.345(1) Å,	O1-O1:	2.8272 Å

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