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**Electronic Supporting Information**

# Robust thermal-energy-storage property associated with electronic phase transitions for quadruple perovskite oxides

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## Experimental details

### Sample Preparation

$R$$Cu_3Fe_4O_{12}$ ($R$ = La, Pr, Nd, Sm, Gd, Dy) was synthesized by a high-pressure method according to the literature.[1] Stoichiometric amounts of rare-earth metal oxides ($R_2O_3$; $R$ = Pr, Nd, Sm, Gd, Dy, 99.9%) or lanthanum nitrate [$La(NO_3)_3 \cdot 6H_2O$ (99.9%)], $Cu(NO_3)_3 \cdot 3H_2O$ (99.9%), $Fe(NO_3)_3 \cdot 9H_2O$ (99.9%) were dissolved into distilled water and stirred in nitric acid with excess amounts of citric acid and ethylene glycol. The mixture was continuously stirred and heated up to 573 K until the solution became a gel, then the gel was dried in the oven at 673 K for 1 h in the air. The obtained gel was grounded and calcined at 1173 K for 10 h under air. The obtained precursor of $R$$Cu_3Fe_4O_y$ ($y$~10.5) and oxidizing agent of $KClO_4$ were mixed at the molar ratio of 4:1, and filled into a platinum capsule. The capsule was put into a octahedral-shaped (Mg, Co)O pressure-transmitting medium and compressed to 8 or 12 GPa by using Walker-type high-pressure apparatus. The capsule was heated at 1073 K for 30 min, then the applied pressure was slowly released. The obtained polycrystalline sample was ground into the powder with mortar and then washed with deionized water several times.

### Characterization

Laboratory X-ray diffraction (XRD) were measured using X-ray diffractometer with Cu K$\alpha$ radiation (Ultima IV, Rigaku, Japan). Synchrotron XRD (SXRD) data were collected at temperatures between 200-400 K for $LaCu_3Fe_4O_{12}$ and $GdCu_3Fe_4O_{12}$ with a Debye-Scherrer camera installed at the BL02B2 beamline of SPring-8, Japan. The powder sample was contained in a Lindemann glass capillary tube with an inner diameter 0.2 mm. The wavelength used was determined to be 0.50020 Å using a $CeO_2$ standard. Structure parameters were refined by Rietveld analysis using the program RIETAN-FP.[2] The crystal structure was drawn using the VESTA-3 software.[3]

Differential scanning calorimetry (DSC) measurement was carried out in a nitrogen gas flow at temperatures between 300–500 K ($LaCu_3Fe_4O_{12}$), 125–500 K ($PrCu_3Fe_4O_{12}$), 125–500 K ($NdCu_3Fe_4O_{12}$), 125–

400 K ($SmCu_3Fe_4O_{12}$), 125–500 K ($GdCu_3Fe_4O_{12}$), 125–400 K ($DyCu_3Fe_4O_{12}$) using DSC7020 (Hitachi High-Technologies, Japan). Heating and cooling rates were fixed at 10 ºC/min. Transition temperatures on heating/cooling process were defined by the endothermic/exothermic peaks in DSC curves. Latent heat capacity was calculated by integrating the area of endothermic/exothermic peaks, where the baseline was estimated by line.

**Table S1.** Transition temperature ($T_t$), specific transition enthalpy ($\Delta H$), and specific transition entropy ($\Delta S$) at heating/cooling process for $R$Cu$_3$Fe$_4$O$_{12}$ ($R$ = La, Pr, Nd, Sm, Gd, Dy).

| $R$ | $T_t$ (K) | $\Delta H$ (J g$^{-1}$) | $\Delta S$ (J g$^{-1}$ K$^{-1}$) |
|---|---|---|---|
| La | 368 / 363 | 25.4 / 25.6 | 0.0689 / 0.0704 |
| Pr | 342 / 331 | 21.4 / 21.2 | 0.0625 / 0.0640 |
| Nd | 334 / 327 | 20.1 / 19.7 | 0.0601 / 0.0600 |
| Sm | 285 / 278 | 19.4 / 19.8 | 0.0682 / 0.0712 |
| Gd | 254 / 235 | 15.0 / 15.3 | 0.0591 / 0.0651 |
| Dy | 227 / 217 | 5.94 / 2.97 | 0.0262 / 0.0137 |

**Table S2.** Refined structure parameters for $LaCu_3Fe_4O_{12}$ and $GdCu_3Fe_4O_{12}$ at room temperature.[a]

| | $LaCu_3Fe_4O_{12}$ | $GdCu_3Fe_4O_{12}$ |
|---|---|---|
| space group | $Im\bar{3}$ | $Im\bar{3}$ |
| $a$ (Å) | 7.42104(7) | 7.33174(2) |
| $y$ (O) | 0.3106(2) | 0.3020(16) |
| $z$ (O) | 0.1704(2) | 0.1757(18) |
| $U_{iso}$(La/Gd) × 1000 (Å$^2$) | 2.3(12) | 3.95(6) |
| $U_{iso}$(Cu) × 1000 (Å$^2$) | 6.0(13) | 5.78(7) |
| $U_{iso}$(Fe) × 1000 (Å$^2$) | 3.5(11) | 2.64(7) |
| $U_{iso}$(O) × 1000 (Å$^2$) | 5.0(4) | 4.8(3) |
| $R_{wp}$ (%) | 7.318 | 6.112 |
| $R_B$ (%) | 2.410 | 1.915 |
| Goodness-of-fit | 0.6374 | 0.6281 |

[a]Atomic site: La/Gd 2*a* (0, 0, 0), Cu 6*b* (0, $^1/_2$, $^1/_2$), Fe 8*c* ($^1/_4$, $^1/_4$, $^1/_4$), O 24*g* (0, *y*, *z*); The occupancy factors *g* for all sites were fixed at the unity.

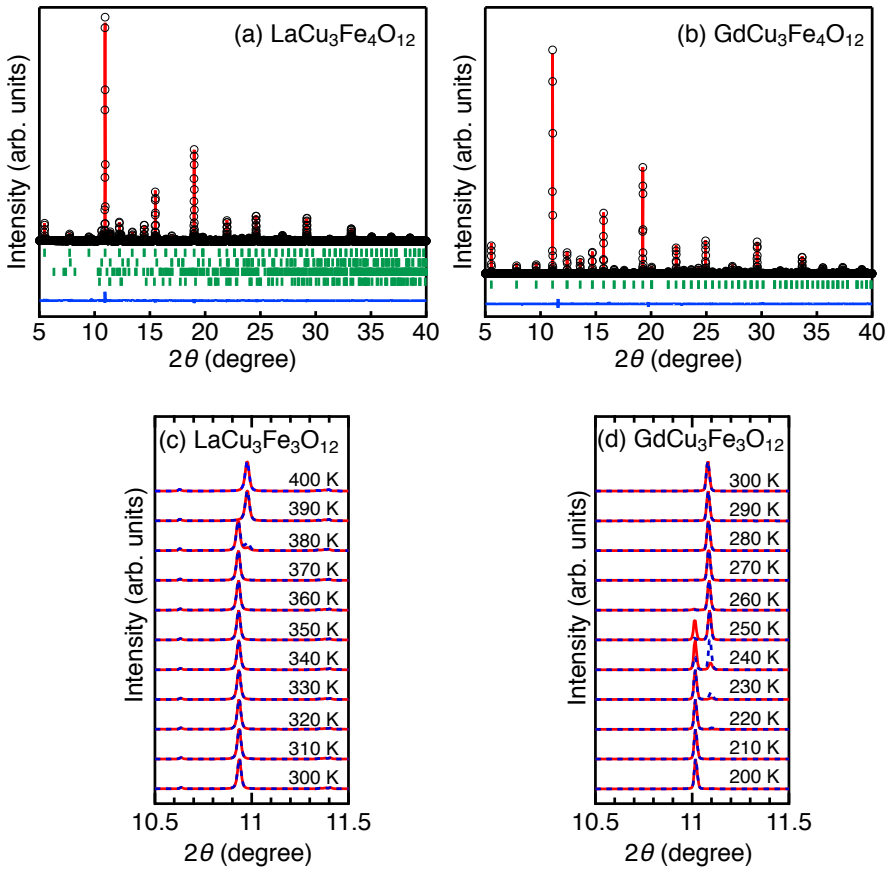


**Figure S1** Rietveld refinement results of SXRD data for (a) $LaCu_3Fe_4O_{12}$ and (b) $GdCu_3Fe_4O_{12}$ at 300 K. The wavelength was 0.50002 Å. Circles (black) and lines (red) indicate observed and calculated SXRD profiles, respectively. The vertical marks (green) indicate the Bragg reflection positions for $LaCu_3Fe_4O_{12}$ (top), $LaFeO_3$ (middle-up), $\alpha$-$Fe_2O_3$ (middle-down), and CuO (bottom) for $LaCu_3Fe_4O_{12}$. SXRD patterns near 110 reflection for (c) $LaCu_3Fe_4O_{12}$ (300–400 K) and (d) $GdCu_3Fe_4O_{12}$ (200–300 K). The solid (red) and dashed (blue) lines represent the profiles on heating and cooling process, respectively.

**References**


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