Supporting information

Lithium ion conduction in a cation deficient quadruple perovskite $LiCuTa_3O_9$ epitaxial thin film: theoretical and experimental investigations

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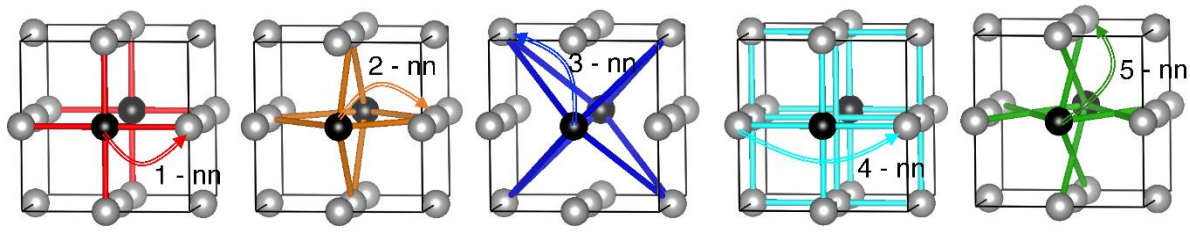

Figure S1. illustrate the nn shell around one of the A' sites which is denoted by black sphere.

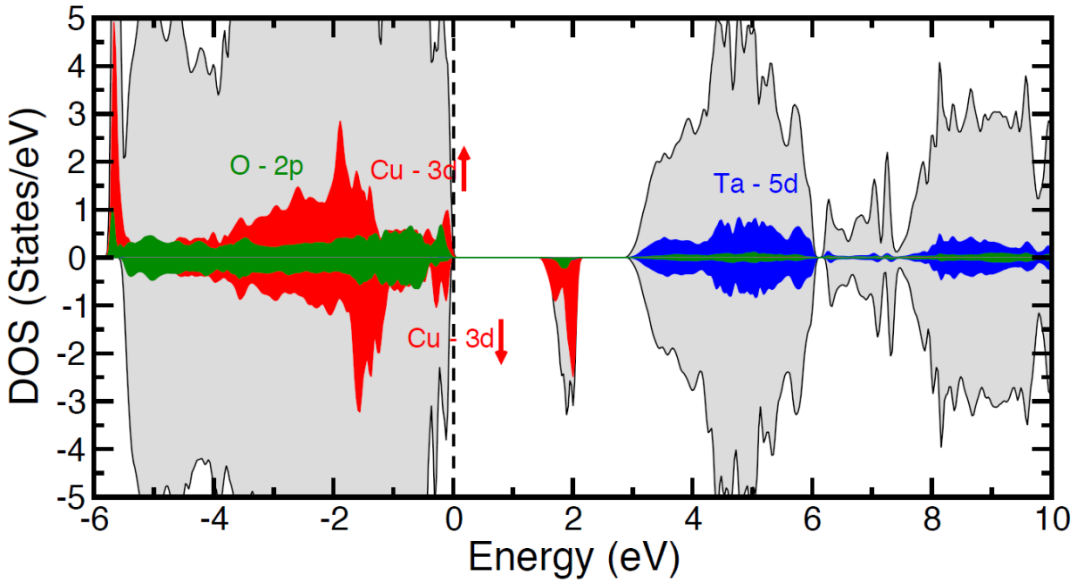

Figure S2. Calculated density of states (DOS) using DFT+*U* method for the most stable cation ordered structure of $LiCuTa_3O_9$.

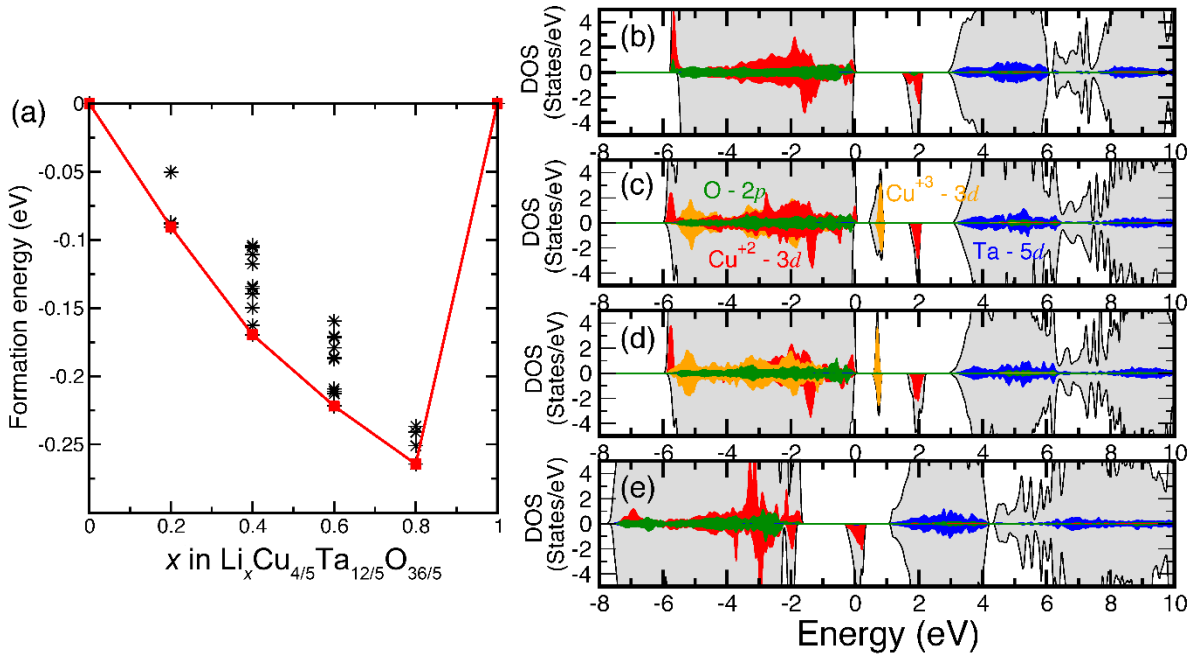

Figure S3. (a) calculated formation energy as a function of Li concentration. (b)-(e) calculated density of states (DOS) of $Li_4Cu_4Ta_{12}O_{36}$, $Li_2Cu_4Ta_{12}O_{36}$, $Li_3Cu_4Ta_{12}O_{36}$ and $Li_5Cu_4Ta_{12}O_{36}$ compositions. These DOS were calculated for the respective lowest energy structures. These DOS were calculated using an effective *U* value of 4.0 eV and 2.0 eV at the Cu 3*d* and Ta 5*d* states, respectively.

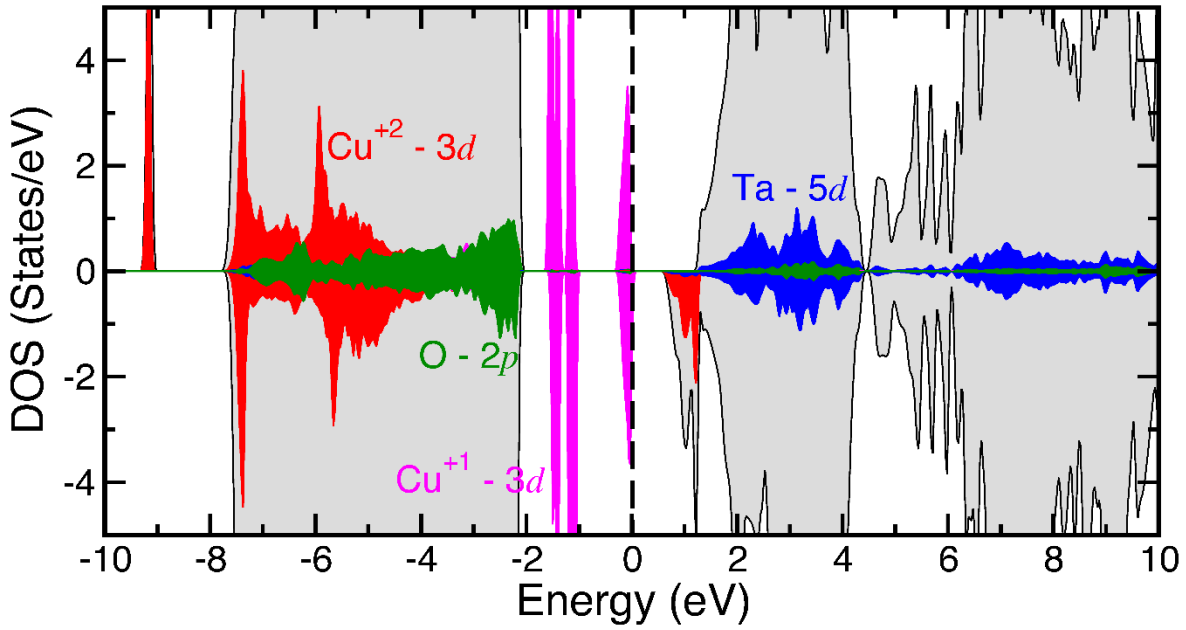

Figure S4. calculated DOS of $Li_5Cu_4Ta_{12}O_{36}$ composition using an effective *U* value of 7.0 eV at the Cu 3*d* state.

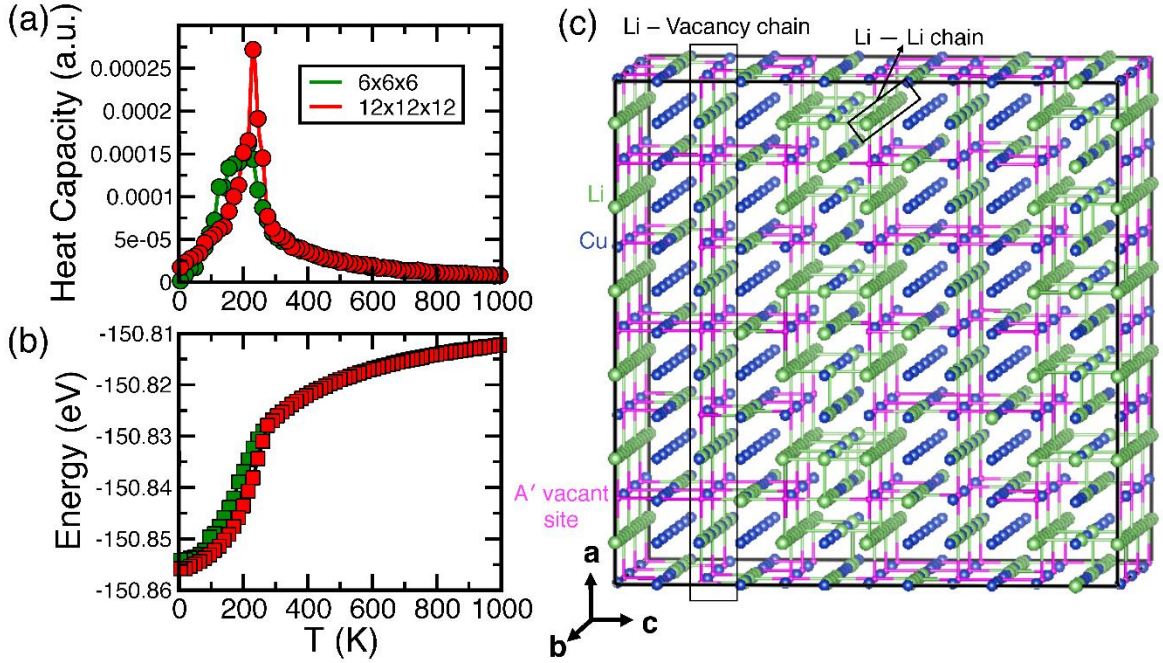

Figure S5. (a) and (b) Calculated specific heat and formation energy as a function of temperature using Monte Carlo method. We show the data calculated with 6x6x6 (648 sites) and 12x12x12 (5184 sites) cell size. We also cross-checked the observed phase transition using $15 \times 15 \times 15$ (10125 A' sites) cell size which also show the phase transition at ~215 K. (c) The structure stabilized at 20 K which shows the key cation ordered features such as, the formation of Li - A'-site vacancy -Li and Li – Li chains, the key features which were also observed in the *Imm2* structure.

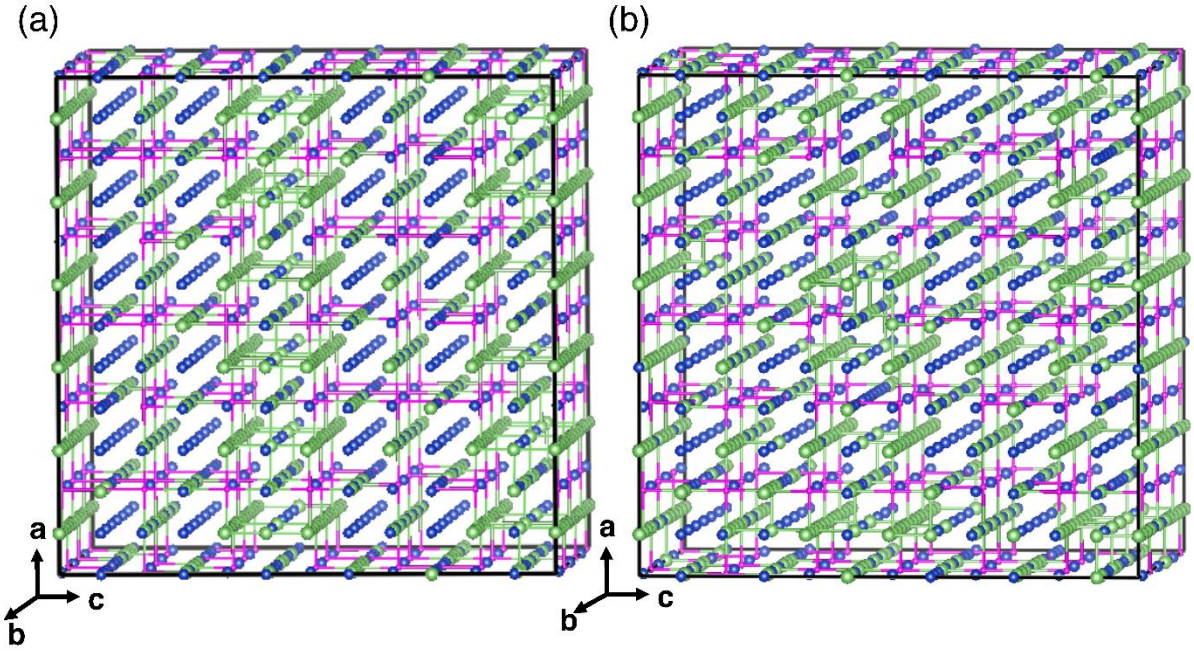

Figure S6. (a) and (b) Structures stabilized at 50 K and 110 K, respectively.