Electronic Supplementary Information

Enhanced thermoelectric performance in ternary spinel $Cu_4Mn_2Te_4$ *via* synergistic effect of tellurium-deficiency and chlorine-doping

Hong Chen,[a] Hua Lin,*, [a] Yi Liu,[b] Xin-Tao Wu,[a] and Li-Ming Wu*, [a, c]

[a] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, People's Republic of China*
[b]*State Key Laboratory of Silicon Materials, School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, People's Republic of China*
[c]*Beijing Key Laboratory of Energy Conversion and Storage Materials, College of Chemistry, Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education, Beijing Normal University, Beijing 100875, People's Republic of China*
** E-mail: linhua@fjirsm.ac.cn and liming_wu@fjirsm.ac.cn.*

Experimental methods

Sample preparation and Property characterization

All of the samples were prepared by solid-state reactions. The weighing manipulation was carried out in an argon-filled glove-box (moisture and oxygen levels less than 0.1 ppm). An approximately total 4 g of reactants (Cu, 5N; Mn, 5N; Te, 5N; $MnCl_2$, 3N, all purchased from Sinopharm Chemical Reagent Co., Ltd.) were mixed and loaded in carbon-coated silica tubes under a residual pressure of ~10^{-3} Pa. The samples were placed into a temperature-controlled muffle furnace, slowly heated to 773 K in 50 h (to aid the volatilizations of raw materials), kept at this temperature for 1 day, and then heated to 1223 K in 30 h, subsequently, annealed at this temperature for 96h. After the furnace cooled to room temperature, the obtained ingots were taken out from the quartz and hand-milled into powders for follow-up hot pressed under 70 MPa at 973 K for 60 minutes in a graphite-steel mold with a 16 mm internal diameter. The obtained pellets were then cut into rectangular pieces of ~ 10 × 3 × 2 mm for electrical

transport measurements, while coins of Φ ~ 10 mm and thickness of ~ 2 mm were used for thermal diffusivity measurements. Seebeck coefficient and electrical resistivity were measured simultaneously in Ultravac ZEM-3 under a helium atmosphere. The thermal diffusivity (D) was measured through laser flash method with Netzsch LFA–457 system. The heat capacity (C_p) was indirectly derived using a representative sample (Pyroceram9606). The total thermal conductivity was calculated via $k = D \cdot C_p \cdot d$, where d was the measured density, which was determined using the dimensions and mass of the sample and then reconfirmed by measurements using Archimedes' principle on a home-built device. All the transport property measurements were performed in the temperature range of 300–773 K. Thermal gravimetric analysis (TGA) scan was measured on a NETZSCH STA 449C simultaneous analyzer under a constant flow of nitrogen gas. Differential scanning calorimetry (DSC) cycling curves were measured by the NETZSCH DTA 404PC with a heating/cooling rate of 5 K/min between 300 and 973 K under an atmosphere of N2. The powder X-ray diffraction (XRD) patterns were taken at room temperature on a Rigaku DMAX 2500 powder X-ray diffractometer by using Cu K_a radiation.

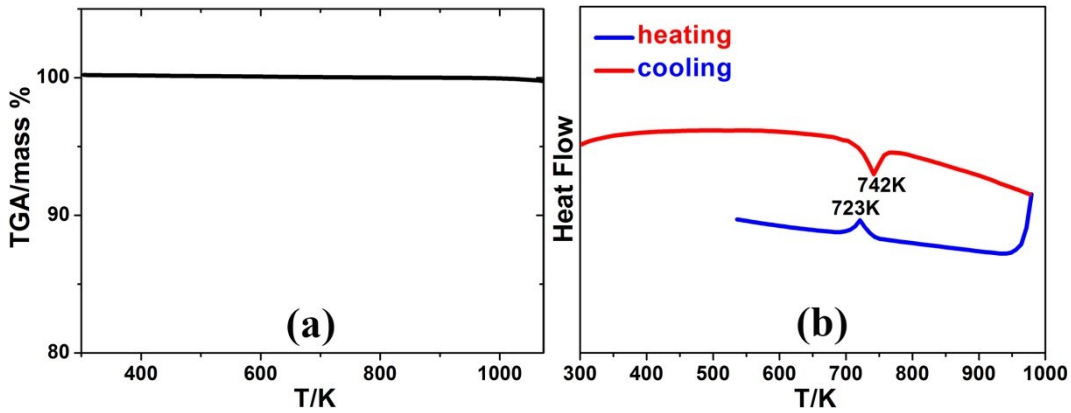

Figure S1. (a) TGA and (b) DSC diagrams of polycrystalline $Cu_4Mn_2Te_4$ sample.

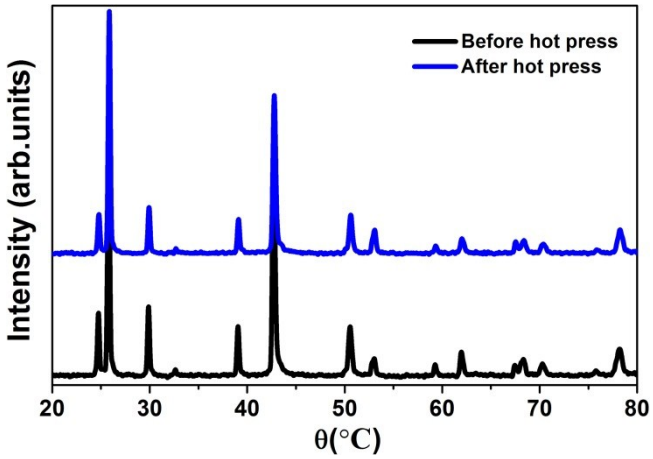

Figure S2. Powder XRD patterns of polycrystalline $Cu_4Mn_2Te_4$ sample before and after hot-pressing.

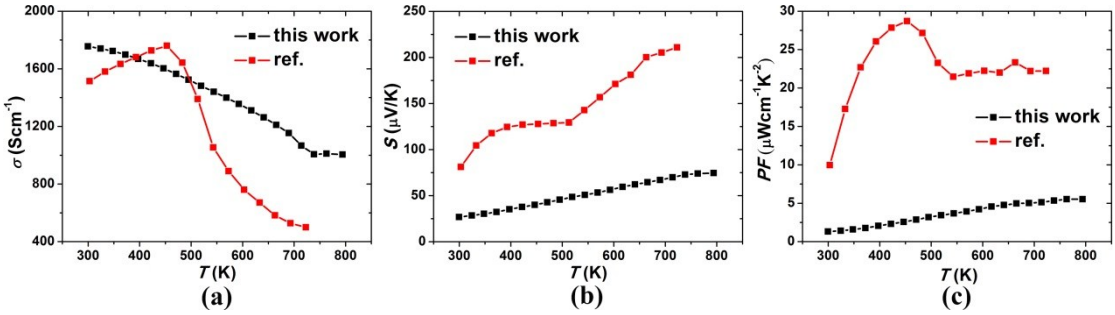

Figure S3. Temperature dependence of the electrical transport properties of polycrystalline $Cu_4Mn_2Te_4$ sample using hot-pressing: (a) electrical conductivity (σ), (b) Seebeck coefficient (S), and (c) power factor ($PF = S^2\sigma$). The data from ref.31 is also shown for comparison.

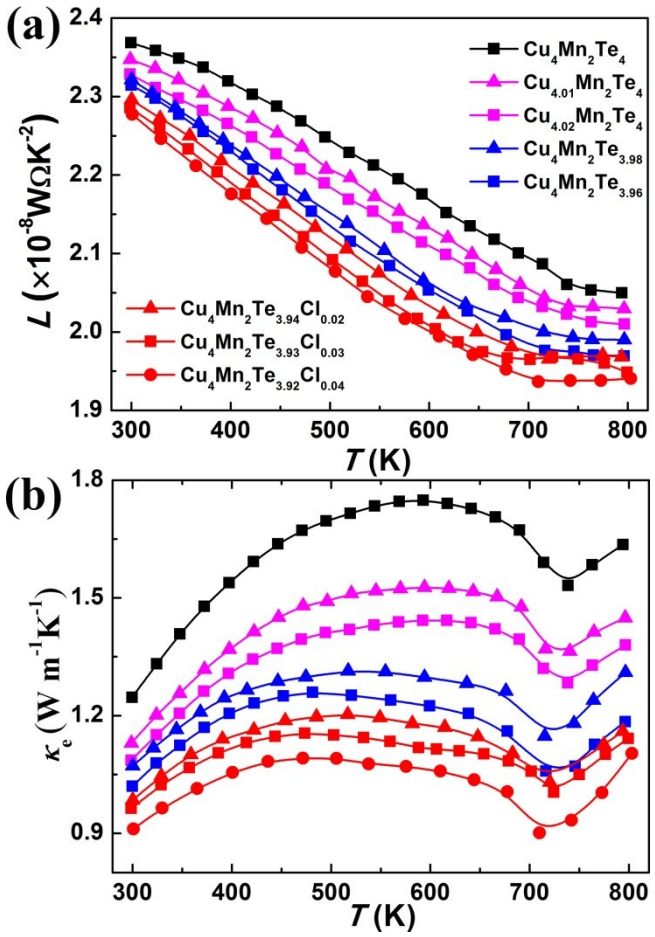

Figure S4. Temperature dependence of (a) Lorenz number (L) and electronic thermal conductivity (k_e) for polycrystalline $Cu_{4+x}Mn_2Te_{4-\delta-y}Cl_y$ samples (x = 0/0.01/0.02, δ = 0, y = 0; x = 0, δ = 0.02/0.04, y = 0; x = 0, δ = 0.04, y = 0.02/0.03/0.04).

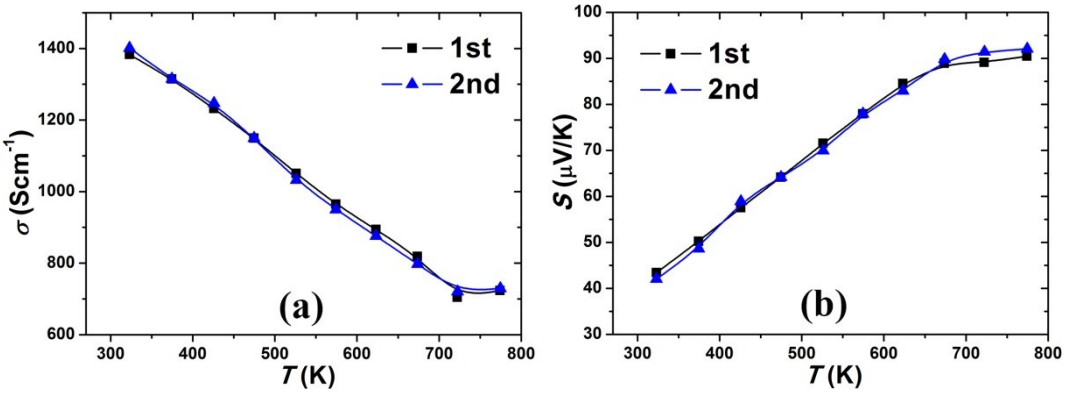

Figure S5. (a) Electrical conductivity (σ) and (b) Seebeck coefficient (S) as a function of the temperature for a hot-pressed polycrystalline sample of $Cu_4Mn_2Te_{3.93}Cl_{0.03}$ during two thermal cycles.