Large latent heat and barocaloric effects at charge transfer transitions of *A*-site ordered perovskite oxides

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An *A*-site ordered perovskite oxide $NdCu_3Fe_4O_{12}$ containing unusual high valence Fe ions shows an intersite charge transfer transition between Cu at the *A'* site and Fe at the *B* site represented by $3Cu^{2+} + 4Fe^{3.75+} \rightarrow 3Cu^{3+} + 4Fe^{3+}$ near room temperature.[1,2] The transition is accompanied by a large volume change as well as metal-to-insulator and paramagnetic-to-antiferromagnetic transitions (Figure 1). We found that the present $NdCu_3Fe_4O_{12}$ released large latent heat 25.5 kJ/kg and the corresponding entropy change 84.2 J/K·kg by the intersite charge transfer transition (Figure 2). We also demonstrated that the latent heat could be utilized through a barocaloric effect by applying pressure.[3]

The observed large entropy change is contributed by the lattice and spin degrees of freedom. The large negative-thermal-expansion-like volume change and the unusual first-order magnetic transition at the charge transition temperature should play important roles in giving rise to the significant entropy change.

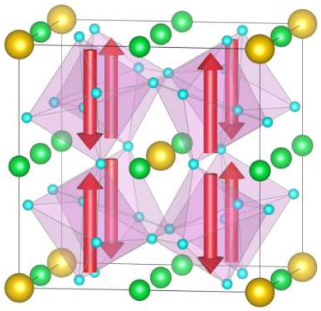

Figure 1 Crystal and magnetic structure of $NdCu_3Fe_4O_{12}$.

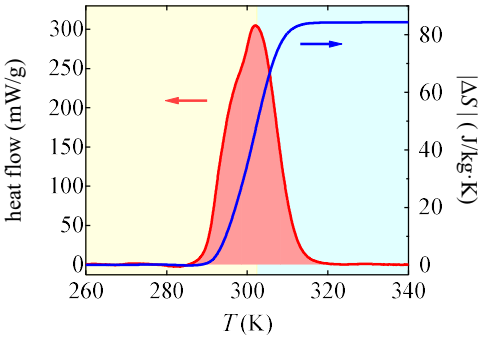

Figure 2 Heat flow and the corresponding entropy change of $NdCu_3Fe_4O_{12}$.

[1] Y. Long, *et al.*, *Nature* **458**, 60 (2009), [2] Y. Shimakawa, *et al.*, *APL Materials* **6**, 086106 (2018), [3] Y. Kosugi, *et al.*, *submitted* (2020)