

Crystal structure analyses of layered thermoelectric manganites

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Perovskite based layered manganites have recently attracted much interest owing to their high n-type thermoelectric (TE) performance at higher temperatures. We have studied the effects of detailed structure, in particular the Mn-O distances and Mn-O-Mn angles, on the TE properties. Here, we report the structure of Sr- and (Bi, Sr)-substituted Ca_2MnO_4 at room temperature; the chemical formulas of the substituted samples are $(\text{Ca}_{1.4}\text{Sr}_{0.5}\text{Bi}_{0.1})\text{MnO}_4$ and $(\text{Ca}_{1.5}\text{Sr}_{0.5})\text{MnO}_4$. Neutron powder diffraction (ND) data were collected at several temperatures by the use of HERMES diffractometer. The ND data were analyzed using the Rietveld refinement program RIETAN2000. In Fig.1(a), we show the observed, calculated and difference patterns of ND data for Ca_2MnO_4 , based on the $I41/acd$ space group. All the samples were refined with the identical space group and converged with reasonably low R-factors. In Fig.1(b), we plot the relationship between the effective ionic radii (R_{eff}) at the Ca site and the Mn-O2 distance as well as the Mn-O2-Mn angles of the MnO_6 octahedra. With increasing R_{eff} , both the dMn-O lengths and Mn-O2-Mn angles increase. The increase in the Mn-O2 lengths reduces the overlapping of the $\text{Mn}3d\text{-O}2p$ orbitals, while the increase in the Mn-O2-Mn angles enhances such overlapping. In fact, the latter effect plays a dominant role to increase TE performance and a further substitution by Sr would be effective to prepare potential n-type TE materials in the Mn-oxides.

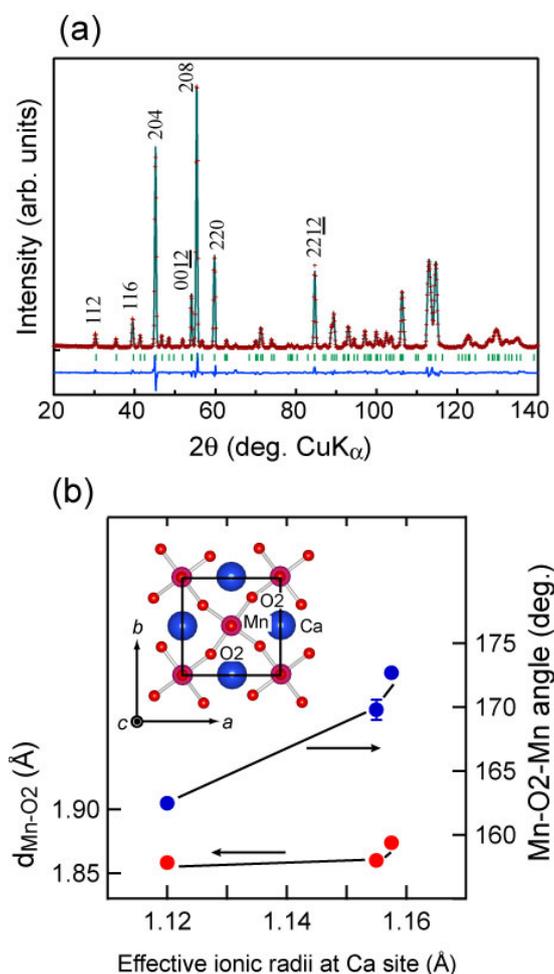


Fig. 1. Rietveld refinement patterns of Ca_2MnO_4 (a) and the relationship between the effective ionic radii (R_{eff}) at the Ca site and the Mn-O2 distances as well as the Mn-O2-Mn angles of the MnO_6 octahedra (b).