Advancements in energy conversion technologies and applications are key goals for the global economy in the new millennium. Oxide materials that have high temperature stability are potential candidates for waste heat energy conversion applications. The phase diagrams of the Ca-M-Co-O (M=Sr, La, Sm, Eu, Gd, Dy and Ho) systems were determined (Fig. 1 gives an example of the phase diagram of the Ca-Sr-Co-O system). These diagrams offer compatibility relationships in the ternary oxide systems that are essential for processing and for the understanding of thermoelectric properties. In these systems, in addition to the well-known (Ca, M)₃Co₄O₉ phase (with misfit layered structure) that has excellent thermoelectric properties, other low-dimensional phases include the homologous series, Aₙ₊₂CoₙCo’O₃ₙ+₃ (where A=Ca, and (Ca, Sr)) (Fig. 2). While the members of the Aₙ₊₂CoₙCo’O₃ₙ+₃ series have reasonably high Seebeck coefficients and relatively low thermal conductivity, the electrical conductivity needs to be increased in order to achieve higher figure of merit (ZT) values. This paper discusses our structure/phase equilibria/property studies of selected cobaltates in the Ca-M-Co-O systems.

Figure 1. Phase diagram of the SrO-CaO-CoOₓ system at 850 °C.

Figure 2. Crystal structure of Ca₃Co₂O₆ (n=1 member in the homologous series, Caₙ₊₂CoₙCoO₃ₙ₊₃).