The main aim of this research is to investigate and develop well-performing p-type thermoelectric oxide materials that are sufficiently stable at high temperatures for power generating applications involving industrial processes. Presently, the challenges facing the widespread implementation of thermoelectric power generation technology lie in the high cost and low efficiency of thermoelectric systems. Scalable and practical applications, including commercialization based on the currently used materials are subject to environmental and cost issues, and thus are difficult to be realized. Metal oxides have attracted much attention due to features such as a natural abundance of constituent elements, environmental benignity and durability at high temperature in air. This research aims to develop and investigate the misfit-layered cobaltate Ca$_3$Co$_4$O$_9$+$\delta$, which demonstrates a large potential for high temperature applications owing to its large positive Seebeck coefficient (S) together with a metallic-like electrical conductivity and a low thermal conductivity typical of a “phonon glass–electron crystal”. The research begins with the study of Ca$_3$Co$_4$O$_9$+$\delta$ syntheses by solid-state and sol–gel reactions, followed by the use of spark plasma sintering (SPS) processing with different conditions such as sintering temperatures, applied pressures and ramping rates. With characterization of the microstructure, bulk density and thermoelectric transport properties, Ca$_3$Co$_4$O$_9$+$\delta$ synthesized by sol–gel reaction followed by the proper spark plasma sintering processing conditions is suggested to be a beneficial means of obtaining high-performance Ca$_3$Co$_4$O$_9$+$\delta$ owing to the resulting smaller particle sizes and enhanced grain alignment. Other than the conventional solid-state reaction and sol–gel methods, a rapid auto-combustion reaction for the synthesis of Ca$_3$Co$_4$O$_9$+$\delta$ nano-powder is developed to realize nanostructuring for enhanced thermoelectric properties. The procedure is a modification of the conventional citrate–nitrate sol–gel method where an auto-combustion process is initiated by a controlled thermal oxidation–reduction reaction. This synthesis produces morphological and compositional homogeneity, and fine, well-defined particle sizes. With determined optimal spark plasma sintering processing conditions, highly dense and beneficially textured Ca$_3$Co$_4$O$_9$+$\delta$ can be fabricated. Introducing extrinsic elements as dopants may exert great influence on the thermoelectric properties. Singly Fe-doped and Fe/Y co-doped Ca$_3$Co$_4$O$_9$+$\delta$ samples synthesized by the newly developed auto-combustion reaction followed by spark plasma sintering processing with the effects of Fe and Fe/Y doping on the high temperature thermoelectric properties (from room temperature to 800 °C) were investigated and discussed. The Fe substitution at the Co-sites effectively reduces the electrical resistivity ( ) while the Seebeck coefficient is influenced only slightly. Y substitution for Ca$_2+$ leads to an increase in the Seebeck coefficient but also in the electrical resistivity. With a proper amount of Fe co-doping, the increase in the electrical resistivity was compensated, and together with the improved Seebeck coefficient the addition of Fe lead to the enhancement of the overall thermoelectric performance. With the aforementioned approach, further investigation has been conducted on rare-earth doping with Ce in Ca$_3$Co$_4$O$_9$+$\delta$ in order to explore the effects on the high temperature thermoelectric properties. With the auto-combustion reaction synthesis followed by spark plasma sintering processing, Ca$_3$-xCexCo$_4$O$_9$+$\delta$ exhibited increasing electrical resistivity and Seebeck coefficient with increasing Ce doping content over the whole measured temperature range, while the in-plane thermal conductivity ( ) was only slightly influenced. Since the introduction of Ce leads to a small decrease in the power factor (PF) but also reduction in the thermal conductivity resulting in the figure-of-merit (ZT) values being similar to the un-doped Ca$_3$Co$_4$O$_9$+$\delta$, the ZT may be enhanced in rare-earth and transition metal (e.g., Ce and Fe) co-doped Ca$_3$Co$_4$O$_9$+$\delta$ through decoupling of the otherwise interdependent electronic and thermal transport properties.