ABSTRACT

Yadav, Gautam Ganapati. Ph.D., Purdue University, Dec 2013. Design and Assembly of Nanostructured Complex Metal Oxide Materials for the Construction of Batteries and Thermoelectric Devices. Major Professor: Yue Wu.

Thermoelectric devices and lithium-ion batteries are among the fastest growing energy technologies. Thermoelectric devices generate energy from waste heat, whereas lithium-ion batteries store energy for use in commercial applications. Two different topics are bound with a common thread in this thesis – nanotechnology! In fact, nanostructuring is a more preferred term for the approach I have taken herein. Another commonality between these two topics is the material system I have used to prove my hypotheses – complex metal oxides.

Complex metal oxides can be used for both energy generation and storage as they are stable at high temperatures, are benign and inexpensive, and are chemically stable. . Nevertheless, complex metal oxide-based materials have drawbacks when they are used in thermoelectric devices. Since they have high thermal conductivities and low power factors, they have lower thermoelectric figures of merit (ZT). This affects their performance as thermoelectric materials. Nanostructuring can solve this critical problem as thermal conductivity, electrical conductivity and Seebeck coefficient become quasi-independent of each other under these conditions. However, oxide-based materials have proven to be greatly recalcitrant to forming nanostructures when traditional synthetic methods such as solid-state reactions have been employed. Solid-state reactions usually proceed at extremely high temperatures that are not particularly conducive to forming nanostructures. The first part of this thesis presents novel solution-based synthetic methods that were developed in order to produce novel nanostructured complex metal oxides. Typical structures include nanowires. The second part

of this thesis extends this methodology to study the effect of nanostructuring on the thermal conductivity of strontium titanate ($SrTiO_3$), a promising high temperature thermoelectric material. Ultrathin nanowires of $SrTiO_3$ were synthesized using a novel hydrothermal reaction. These ultrathin nanowires were compressed into a 'nanostructured' bulk pellet through spark plasma sintering. The thermal conductivity measured on the nanostructured bulk pellet showed a drastic decrease compared to bulk $SrTiO_3$. Through theoretical modeling it was realized that drastic decrease in thermal conductivity was due to scattering of phonons, which contribute to the lattice thermal conductivity, at the interface of the nanowires.

Another aspect of the thermoelectric research presented herein includes the development of a new phase of misfit layered oxide, calcium cobalt oxide ($Ca_9Co_{12}O_{28}$), for high temperature applications. This phase had hardly been researched in literature because of its high thermal conductivity, thus limiting its use in thermoelectric devices. Through a unique single source precursor-based technique, porous nanowire structures of $Ca_9Co_{12}O_{28}$ were prepared at much lower temperatures than conventional solid-state techniques. Significantly improved ZT were observed in our nanowire system up to 700K due to reduced thermal conductivity and enhanced Seebeck coefficient. The synthetic approach was also applied to prepare different nanostructures (porous nanowires and nanoparticles) of lithium cobalt oxide ($LiCoO_2$) by tuning individual reaction parameters. The importance of reaction temperature and the role of nanostructures on the final electrochemical performance of $LiCoO_2$ was also deduced. Saliently, the nanostructured electrodes so prepared can withstand high cycling rates and achieve capacities that are close to the theoretical capacity of $LiCoO_2$ at 0.1C.