**Synthesis and characterizations of layered cobalt oxides ACoO2 (A=Na, Li, Pt and Pd) for thermoelectric applications**

Thermoelectric materials are the materials that can convert heat into electricity and vice versa. The generated electricity depends on the temperature gradient as well as property of the material. It can be explained by two different effects, Seebeck effect and Peltier effect. :Jonn Seebeck 1821 found that a voltage existed between two ends of a metal bar when a temperature gradient, ΔT, existed in the bar. When a closed loop is made of two metals with a temperature difference, a potential difference is induced. The figure of merit for thermoelectric material is given by

Z= S2 σ / k (1)

Where S is seebeck coefficient, σ is electrical conductivity and k is thermal conductivity of the material. Dimensionless figure of merit is given by

ZT= ( S2 σ / k )(T1+T2)/2 (2)

For better power factor the material should have the bellow properties a material should have high electrical conductivity, high seebeck coefficient and low thermal conductivity since these parameters are functions of carrier concentration, they cannot be controlled independently. Thus, large ZT is very difficult to realize. ZT takes a maximum around unity in conventional thermoelectric materials, though ZT > 3 is needed to compete with a gas-compressor-based refrigerator. ZT=1 is suitable for thermoelectric applications. The current state of the art materials include Bi2Te3; ZT=0.9 at room temperature, PbTe; ZT=1.2 at 700°K and SiGe; ZT=0.6 at 1000°K. Oxide materials had been ignored for a long time by the thermoelectric community, but the discovery of NaxCoO2 as a strong candidate thermoelectric material. It was found that layer-structured Oxide NaxCoO2 was a highly effective thermoelectric material, and the dimensionless figure of merit ZT of single crystal of Na0.7CoO2 was shown to exceed unity, which is a standard value for practical applications. After this discovery the layered cobalt oxides attracted the scientific community to study and to improve the properties towards thermoelectric applications.

The layered sodium cobalt oxide was synthesized using hydrothermal synthesis method. For the first step, we studied the Co-NaOH-H2O system for the temperature region 1500C-2500C, molality of NaOH from 1m to 4m and synthesis time for 24h and 60h. The resultant samples show different phases at different synthesis conditions. Effect of hydrogen peroxide is studied at higher molality of NaOH solutions; 1800C, 2200C and 2500C. Pure phases (XRD) of layered sodium cobalt oxides synthesized at 2200C with higher molality of NaOH and in the presence of hydrogen peroxide. The samples were characterized by X-ray diffraction and EDAX. The evolution of phases with cleaning process was observed might be due to unstable state of Co4+. The structural refinement of the powder X-ray diffraction shows *R3m* space group with lattice parameters as a= 2.8312 Å, and c= 16.5915 Å . The phase transformation from *R3m* to *R-3m* was observed above 4500C.

Polycrystalline LiCoO2 was synthesized using Co(OH)2 and LiOH were the precursors, NaOH as ionic mineralizer and 5% H2O2 as oxidizing agent in soft hydrothermal conditions. The effect of ionic mineralizer was studied by varying the NaOH/LiOH ratio by keeping rest of the parameters fixed. The structural refinement for powder X-ray diffraction pattern shows R-3m space group with lattice parameters a=b=2.81547 Å and c= 14.0635 Å .The morphology of the samples differ for different synthesis conditions, it varies from desert rose to concaved cuboctahedrons either with higher synthesis times or with specific ratios of ionic mineralizers used . The susceptibility measurements of the samples show Curie-Weiss behavior. And then the EPR measurements show a very small impurity from nickel that might be from the precursor. The effect of ionic mineralizers and the concentration of precursor were studied to optimize the synthesis conditions of LiCoO2: i) for low mineralizers concentration, only cobalt oxides form; ii) as the concentration increases., pure LiCoO2 grows; iii) the crystallinity of the compound increases as the ratio NaOH/LiOH increases; iv) the Co(OH)2 concentration threshold is *ca.* 50mmol/l; bellow this limit a single phase LiCoO2 grows and above, Co(OH)2 re-crystallizes . In the reaction time window 24-60 h was able to stabilize CoO free concave cuboctahedrons particles suggesting that an alternative mechanism for the growth of these particles should be considered. Magnetic measurements (local and macroscopic) highlight the presence of cobalt oxides impurities which amount is decreasing (and nearly vanishes) with reaction time; they also reveal, as already observed, the presence of several kind of close to surface centers .LiCoO2 was obtained at lower synthesis parameters compared to the available literature, the structural, morphological, and magnetic properties were studied.

Polycrystalline samples of NaxCo1-y MgyO2 were synthesized using Na2CO3 and Co1-xMgxO were the starting materials in conventional solid-state reactions. The precursors were well grinded and thermally treated at 9000C for 24h with continuous flow of oxygen and subsequently pelletized and sintered at 9000C during 24h in oxygen atmosphere. This new approach can open the window for divalent substitutions in other alkaline cobalt oxides. The samples show P2-polytype (*P63/mmc*) and the lattice parameters increases with Mg substitution rate. The linear variation of susceptibility with temperatures shows that all the samples show Curie-Weiss behaviour. The resistivity of all the samples shows strong metallic behaviour with temperature, the temperature coefficient of resistivity is in the order of 10-3/K. The seebeck measurements shows the contribution from spin entropy and obeying the strong correlation effects; contribution from degeneracy of octahedral distortions.

The crystals of Pt(CoMg)O2 were grown using PtCl2, CoO or alternatively Co1-xMgxO for the substituted samples in metathetical reactions in vacuum sealed quartz tubes at 7000C for 40h with heating rate keeping at 1.50C/min and the cooling rate at 10C/min. The profile matching with FULL PROOF program for the power X-ray diffraction patterns represents that the crystals obtained were with 3R polytype (*R-3m*). The lattice parameters show an increment with respect to the Mg substitution rate due to higher radius of Mg2+ compared to Co3+. The morphology of the crystals shows plate like 2D hexagonal shape. The EPMA analysis shows the approximate Co:Mg for lower Mg substitution rate and the optimal value was found around 7.5 . The variation of susceptibility with temperature shows Curie-Weiss behaviour. The Curie constant, Curie temperature and temperature dependent susceptibility were determined by means of Curie-Weiss law. The %s1/2 was calculated with the assumption that the Co4+ is in LS state (spin=1/2). The deviation of these values shows the deficiency in Pt-layer . In general divalent substitutions in delafossite compounds were shown to be limited at low rates, where the individual precursors for each cation were taken. The present study reveals the higher level substitutions; Mg substitution rate exceeds 5% which is much higher compared to divalent substitution in any delafossite compounds in the available literature.

The single crystals of Pd(CoMg)O2 were grown using PdCl2, CoO or alternatively Co1-xMgxO for the substituted samples in metathetical reactions in vacuum sealed quartz tubes. The larger crystals were obtained by the following thermal treatment; heating the vacuum sealed quartz tube to 930 °C in 2 h, then 1000 °C in 6 h; fast cooling to 580 °C in 1‑2 h; heating to 700 °C in 2 h with a dwell of 40 h; final cooling to RT at the rate of 40 K/h). The single crystals were finally cleaned with ethanol and distilled water to get rid of by products. The crystals show 3R-polytype (R-3m) and the lattice parameters increases with increasing Mg substitution rate . The single crystal X-ray diffraction confirms that the crystals obtained were single crystals . The obtained single crystals were larger in dimensions with 2D growth. The susceptibility measurements show Curie-Weiss behaviour. The %s1/2 was calculated with the assumption that the Co4+ is in LS state (spin=1/2). These results show the high-level Mg substitution at Co-site. The single crystals show metallic behaviour, and the resistivity was changed by one order in magnitude with Mg substitution. The crystals show huge anisotropy in resistivity measured along ab-plane and c-axis directions. The residual resistivity is about 405 (*ρ*(300K)/ *ρ*(4K)) and 2.8 for 20% of Mg substituted samples along ab-plane and c-axis directions respectively. The XPS spectra shows the existence of Pd2+ with Mg substitution, it can be concluded that the substitution of Mg creates hole in Pd-layer instead of Co-site. These results suggest the enhancement of Mg substitution rate using binary oxide as precursor. This approach might impact several divalent substitutions in ABO2 compounds.