

# Chemical design of layered cobaltites for thermoelectric applications

Berthelot R.<sup>1</sup>, Pollet M.<sup>1</sup>, Carlier D.<sup>1</sup>, Decourt R.<sup>1</sup>,  
Doumerc J.-P.<sup>1</sup>, Delmas C.<sup>1</sup> and Plissonnier M.<sup>2</sup>

<sup>1</sup> Université de Bordeaux, ICMCB, 87 avenue du Dr. Schweitzer, F-33608 Pessac, France

<sup>2</sup> CEA-Grenoble, DRT-LITEN, 17, rue des Martyrs, 38054 Grenoble, France

Contact author : pollet@icmcb-bordeaux.cnrs.fr

## Abstract

Mixed layered cobaltites  $\text{Li}_x\text{Na}_y\text{CoO}_2$  have been prepared and characterized. Preliminary results on physical properties are presented and discussed.

## Introduction

Layered cobaltites  $\text{A}_x\text{CoO}_2$  have been intensively studied as cathode materials [1,2]. More than 20 years ago, a positive thermoelectric power of  $80 \mu\text{V}\cdot\text{K}^{-1}$  and a low electrical resistivity of  $3 \text{ m}\Omega\cdot\text{cm}$  at 300 K were reported for a powder sample  $\text{Na}_{0.7}\text{CoO}_2$  [1,2]. More recently an in-plane power factor value close to that of  $\text{Bi}_2\text{Te}_3$  at 300 K has been reported for single crystals of the same composition [3] triggering a renewed interest for these materials.

Good thermoelectric properties require conflicting features: a large Seebeck coefficient ( $\alpha$ ), a small electrical resistivity ( $\rho$ ) and a low thermal conductivity ( $\kappa$ ), in order to improve the figure of merit  $Z\cdot T = \alpha^2 / \rho\kappa$ . Two contributions occur in the thermal conductivity, an electronic contribution ( $\kappa_e$ ) and a phononic contribution ( $\kappa_{ph}$ ).

As  $\kappa_e$  is directly related to the electrical resistivity by the Wiedemann-Franz law, it cannot be significantly decreased without increasing  $\rho$ . Hence dropping  $\kappa_{ph}$  is required in order to improve  $Z\cdot T$ . This approach has been already applied to systems like skutterudites or clathrates and our purpose is to extend it to cobaltites. Our strategy is to limit the phonon mean free path through introducing a random mixture of elements in the alkali layers. Our study is focused on the mixed layered

cobaltite  $\text{Li}_x\text{Na}_y\text{CoO}_2$  for which promising thermoelectric properties were recently reported [4-5]. In the present paper after briefly reviewing the state of the art concerning these cobaltites, synthesis and preliminary Seebeck and electrical resistivity measurements are presented and discussed. Thermal conductivity will be considered in a future work.

## State of the art of the $\text{Li}_x\text{Na}_y\text{CoO}_2$ system

Balsys *et al.* [6] reported synthesis of  $\text{Li}_{0.43}\text{Na}_{0.36}\text{CoO}_2$  using a two-step solid state method from an equimolecular mixture of  $\text{Na}_{0.7}\text{CoO}_2$  and  $\text{LiCoO}_2$  heated in air at 1123 K for 4 days. More recently Ren *et al.* [4] reported the direct synthesis of  $\text{Li}_{0.48}\text{Na}_{0.36}\text{CoO}_2$  from  $\text{Li}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$  and  $\text{Co}_3\text{O}_4$  (30 hours at 1173 K under oxygen flow followed by annealing at 673 K for one day). Ren *et al.* also reported interesting thermoelectric properties for a polycrystalline sample at room temperature:  $\alpha=180 \mu\text{V}\cdot\text{K}^{-1}$ ,  $\rho=20 \text{ m}\Omega\cdot\text{cm}$  and  $\kappa=2 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ , which leads to a ZT of 0.02. Last year Bos *et al.* [5] studied magnetic and thermoelectric properties of several materials prepared from deintercalation of sodium or lithium from an initial thermodynamical stable phase  $\text{Li}_{0.41}\text{Na}_{0.31}\text{CoO}_2$ .

All the authors have reported the same crystallographic structure for this mixed cobaltite. It consists of stacking of layers of edge-sharing  $\text{CoO}_6$  octahedra between which the alkali ions are inserted. The alkali ions can accommodate two main types of crystallographic sites: either octahedral (O) in  $\text{Li}_x\text{CoO}_2$  or prismatic (P) in both  $\text{Na}_x$ - and  $\text{K}_x\text{CoO}_2$ . The oxygen packing also differs in the number of

sheets within the pseudo-hexagonal unit cell. The O3 phase is isostructural with  $\alpha$ -NaFeO<sub>2</sub> and AO<sub>6</sub> octahedra are sharing only edges with CoO<sub>6</sub> octahedra. In P3, AO<sub>6</sub> prisms are alternatively sharing edges and faces with lower and upper CoO<sub>6</sub> octahedra. The P2 system features two distinct types of AO<sub>6</sub> prisms: the first one is sharing only faces and the second one is sharing only edges with CoO<sub>6</sub> octahedra.

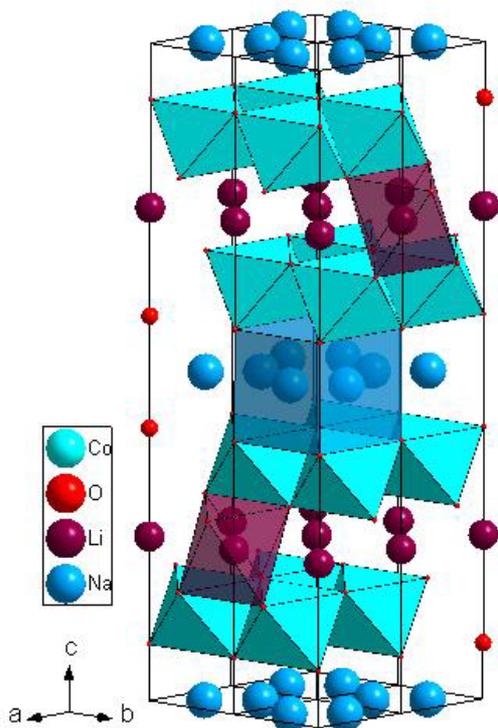


Figure1: Crystal structure of  $\text{Li}_x\text{Na}_y\text{CoO}_2$ .

In the Li/Na mixed cobaltites crystallographic features of lithium and sodium cobaltites are combined. Interslabs between the sheets of edge sharing CoO<sub>6</sub> octahedra are alternatively filled by sodium or lithium layers. Figure 1 shows the corresponding structure.

### Preparation and characterization

According to previous works it is very challenging to obtain a pure phase. Thus Balsys *et al.* noticed that LiCoO<sub>2</sub> remained in the final product. Ren *et al.* sometimes observed LiCoO<sub>2</sub> or Na<sub>x</sub>CoO<sub>2</sub> impurities. Taking into accounts these difficulties, we tuned the condition of synthesis in order to improve the phase purity. Our best results

were obtained in grinding together LiCoO<sub>2</sub> and Na<sub>0.7</sub>CoO<sub>2</sub> in the nominal composition of Li<sub>0.42</sub>Na<sub>0.41</sub>CoO<sub>2</sub>. Manipulations are made in an argon-filled glove box. The mixture is then put in a gold tube that is the sealed and heated at 1193 K during 15 hours in a pre-heated furnace. The tube is finally quenched in water and the product is stored under dry argon atmosphere to prevent moisture contamination.

XRD patterns were recorded with a Panalytical X'Pert Pro powder diffractometer in the Bragg-Brentano geometry using Co K<sub>α</sub> radiations. All the XRD peaks can be indexed using a hexagonal cell and the P6<sub>3</sub>mc space group. Refined lattice parameters are a=2.829 Å and c=20.286 Å, which is in good agreement with previous works.

The measurements of thermopower and electrical resistivity were carried out on cylindered pellets with compactness close to 89%. Electrical DC-conductivity measurements were performed using a four probe method in the 4-300 K temperature range. Thermoelectric power measurements were carried out with a home made equipment previously described [7].

### Results and discussions

The temperature dependences of the Seebeck coefficient and of the electrical resistivity are compared with the previous results of Ren *et al.* in Figure 2. The thermal activation of the electrical conductivity denotes a semi-conductor behavior, either of band-type with a thermally activated carrier creation, or a hopping-type semi-conductor with activated carrier mobility. At low temperature, the Seebeck coefficient increases and exhibits a maximum around 200 K then it very slightly decreases. This behavior significantly differs that reported by Ren *et al.* (Fig.2). It supports the second hypothesis at least for 0<T<200 K. The decrease of the thermoelectric power above 200 K could result from a tiny increase of

charge carrier concentration whose the origin is not still explained. Assuming an average oxidation state of cobalt from nominal composition, Heikes formula leads to thermoelectric power values of either 196 or 136  $\mu\text{V.K}^{-1}$  depending whether spin degeneracy is taken into account or not. As the experimental value is close to 150  $\mu\text{V.K}^{-1}$ , no conclusion about the role spin degeneracy can be definitely drawn.

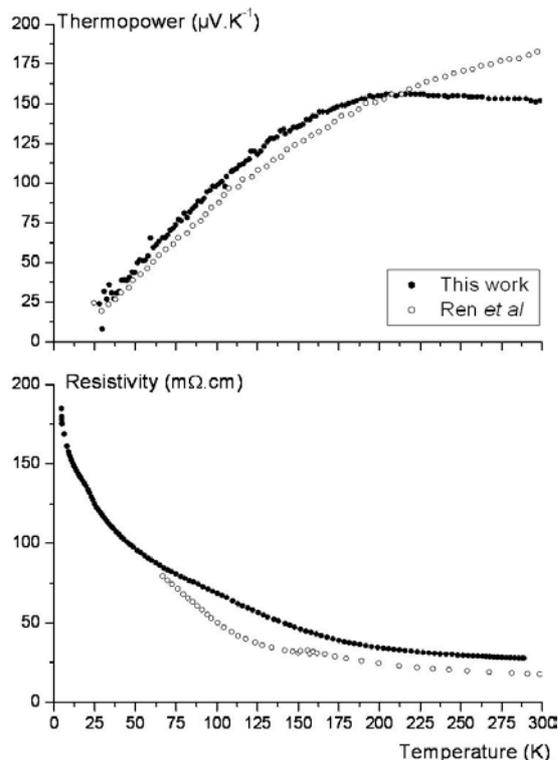


Figure 2: Temperature dependence of Seebeck coefficient and electrical resistivity

Room temperature values of Seebeck coefficient ( $\approx 150 \mu\text{V.K}^{-1}$ ) and electrical resistivity ( $\approx 30 \text{m}\Omega.\text{cm}$ ) lead to a power factor  $\alpha^2/\rho$  close to  $7.5 \times 10^{-2} \text{W.m}^{-1}.\text{K}^{-2}$ .

### Conclusions and outlooks

Since Terasaki focused on the promising thermoelectric properties of  $\text{Na}_{0.7}\text{CoO}_2$ , other layered thermoelectric cobaltites have been reported such as misfit compounds and the Li/Na mixed layered cobaltites discussed in this paper. Previous works pointed out the difficulties to obtain this phase pure. By tuning all the synthesis

parameters, we obtained samples with good purity which is required for an accurate physical characterization.  $\text{Li}_{0.42}\text{Na}_{0.41}$  exhibits a high thermoelectric power of  $150 \mu\text{V.K}^{-1}$ . Keeping in mind that dropping the phononic part of the thermal conductivity is of major importance to improve the figure of merit, the present study should be considered as a preliminary step towards further studies. Actually, many ion exchanges are possible in layered cobaltites that could lead to further improvement of the thermoelectric properties.

### Acknowledgements

This study was supported by the Centre National de la Recherche Scientifique (CNRS), the Commissariat à l'Énergie Atomique (CEA) and the French National Research Agency (ANR) in the scope of the OCTE project.

### References

- [1] Molenda J., Delmas C., Hagenmuller P., *Solid State Ion.*, **9-10**, 431 (1983)
- [2] Molenda J., Delmas C., Dordor P., Stoklosa A., *Solid State Ion.* **12**, 473 (1984)
- [3] Terasaki I., Sasago Y., Uchinokura K., *Phys. Rev. B* **56**, 12685 (1997)
- [4] Ren Z., Shen J., Jiang S., Chen X.-Y., Feng C., Xu Z.-A., Cao G.-H., *J. Phys.: Cond. Mat.* **18**, 379 (2006).
- [5] Bos J.W.G., Hertz J.T., Morosan E., Cava R.J., *J. Solid State Chem.* **180**, 3211 (2007)
- [6] Balsys R.J., Davis R.L., *Solid State Ion.* **69**, 69 (1994)
- [7] Dordor P., Marquestaut E., Villeneuve G., *Rev. Phys. App.* **15**, 1607 (1980)