

Sodium ion mobility in Na_xCoO_2 ($0.5 < x < 1$) cobaltites studied by ^{23}Na MAS NMR

Dany Carlier, Maxime Blangero, Michel Ménétrier, Michaël Pollet, Jean-Pierre Doumerc and Claude Delmas

ICMCB, CNRS Université Bordeaux 1
87 Av. du Dr. A. Schweitzer, 33608 Pessac cedex (France)

In the 80's, Na_xCoO_2 has been widely investigated as potential electrode materials for sodium batteries in our laboratory [1-2]. More recently the Na_xCoO_2 gained a renewed interest because these phases exhibit unusual properties for different x values, in particular enhanced thermopower for $x \sim 0.85$ [3]. Depending on their synthesis condition and Na content the Na_xCoO_2 phases can exhibit different alternate stackings of edge-shared CoO_6 octahedra slabs and of partially vacant alkali layers. In this study we focused on the P2- Na_xCoO_2 ($0.5 < x < 1$) and P'3- $\text{Na}_{0.6}\text{CoO}_2$ phases. We recently showed that the P'3- $\text{Na}_{0.6}\text{CoO}_2$ phase undergoes a phase transition just above room temperature that is associated to an order/ disordering of the Na cations in the interslab space, which leads to a hexagonal not distorted P3- Na_xCoO_2 cell (S.G. R3m).

To our knowledge, this is the first ^{23}Na MAS NMR study of the Na_xCoO_2 ($0.5 < x < 1$). Other groups studied the P2 compounds as single crystal or aligned powder with broad line type NMR spectrometers. In these studies Na^+ ions are said to be mobile from ~ 200 -250 K [4-5] However, we show by variable temperature ^{23}Na MAS NMR, that Na^+ ions are not fully exchanged at room temperature and that the motion is activated upon heating. Depending on the CoO_2 stacking sequence: P2 versus P3 phases, the shape of the exchanged signal is clearly different and will be discussed in relation with the different prismatic Na^+ sites in the structures and the ionic motion pathway.

References:

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E-mail Presenting Author : carlier@icmcb-bordeaux.cnrs.fr