Thermodynamic and transport properties of nanocrystalline and microcrystalline calcium-doped cobalt oxide

L. Cieniek\textsuperscript{1}, J. Kusinski\textsuperscript{1}, G. Baldinozzi\textsuperscript{2}, C. Petot\textsuperscript{2}, G. Petot-Ervas\textsuperscript{2}

\textsuperscript{1}AGH-University of Science and Technology in Cracow, Mickiewicza av. 30, 30-059 Cracow
\textsuperscript{2}Laboratoire SPMS UMR 8580 – CNRS, École Centrale Paris, Grande voie des Vignes 92295 Châtenay-Malabry cedex

We synthesized dense CoO - doped (0.5 mole %) CaO polycrystals, with densities greater than 95 % of the single crystal value, and with grain sizes of approximately: 5÷20 nm (samples C), <5 µm (samples B) and >300 µm (samples A), in order to determine whether the thermodynamic and defect properties of nanocrystalline samples fundamentally differ from those of conventional materials, like (Co,Ca)O single crystals. For samples C (Fig. 1c), obtained from doped nanopowders (prepared by ball milling process) and sintered by PPS technique \cite{1}, the electrical conductivity measurements (Fig. 2a) have been performed at temperatures lower than 900°C, to prevent a grain size increase. Used \textit{Pulsed Plasma Sintering} technique, with short (100 ms) temperature “jumps” under pressure, allowed to avoid grain’s overgrowth. A decrease of the electrical conductivity was observed for $p_{O_2} \approx 10^{-3}$ atm, in agreement with results obtained with single crystals \cite{2}. Furthermore, for oxygen pressures lower than $10^{-3}$ atm, the electrical conductivity plots as a function of $p_{O_2}$ crossover each other (Fig. 2b). Beyond the intersection, the conductivity being a decreasing function of $T$, the enthalpy of formation of the defects is negative. This result indicates that the point defect structure is dominated by the large defect aggregates in the low $p_{O_2}$ range (like 4:1 clusters, formed from one Ca\textsuperscript{2+} interstitial and four singly ionised cobalt vacancies). For samples B and A (Fig. 1a,b), the electrical conductivity measurements have been performed in the temperature range 1000÷1300°C. The values are close to those obtained with a single crystal of CoO - doped with (0.26 mole %) CaO (Fig. 3) \cite{2}. Furthermore, we have found that short circuit effects occur at oxygen partial pressures all the more higher than the grain size increases ($p_{O_2} \approx 10^{-3}$ atm sample A and $p_{O_2} \approx 10^{-9}$ atm sample B, at 1100°C, for instance), while such effects where not observed in nanocristalline samples. These results are consistent with EDS analyses which revealed an enrichment of calcium near the grain boundaries \cite{3}. Indeed, taking into account both that the segregation of dopant near the grain boundaries increases with the grain size, and that the dissociation density of Ca - doped CoO increases with the amount of calcium, the influence of the grain size on the short circuit effects can then be due to an enhanced calcium concentration near the grain boundaries. The explanation of this effect can be supported by the previous results obtained for yttrium-doped zirconia \cite{4}.

On the other hand, optical and TEM examinations coupled to X-ray characterizations performed at high temperature, allowed us to confirm that calcium favours the precipitation of Co\textsubscript{3}O\textsubscript{4}, which occurs near 1110°C in CoO - doped (4.43 moles %) CaO samples, while the precipitates appear only near 910°C in pure CoO.
Fig. 1. Microstructures of (Co,Ca)O polycrystals (a, b) and (Co,Ca)O nanocrystalline sample (c)

Fig. 2. Influence of the oxygen activity and temperature conditions on the electrical conductivity of nanocrystalline sample (a); results compared with CoO–doped (0,26% mole) CaO single crystal (b)

Fig. 3. Influence of the oxygen activity on the electrical conductivity of polycrystals compared with CoO–doped (0,26% and 0,84% mole) CaO single crystals, at 1100°C