Electrochemical characterization of mixed-conducting (Ca,La,Sr)(Co,Mn)O_3

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In intermediate temperature solid oxide fuel cells the slow kinetics of the reduction of oxygen at the cathode side is responsible for most of the resistive losses.[1] The perovskites with the general notation of (Ca,La,Sr)(Co,Mn)O_3 are interesting candidates for new improved cathode materials. Therefore, the aim of this work is the investigation of their electrical properties, their oxygen exchange kinetics and their diffusion process. Firstly bulk samples were prepared and thin films grown by PLD at various oxygen background pressures on $LaAlO_3$ and $SrTiO_3$ single crystal substrates. Subsequently Van der Pauw method was used to quantify the bulk resistivity. For the determination of the oxygen diffusion and surface exchange coefficients, $^{18}O_2$ exchange experiments and subsequent depth profile measurements, using ToF-SIMS, were performed.

Perovskite Crystal Structure

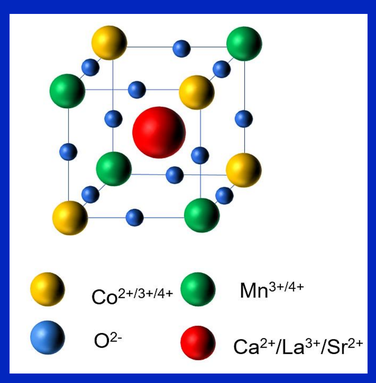

Fig.1: (Ca,La,Sr)(Co,Mn)O_3 crystal structure.

B-site ordering in $LaCo_{0.5}Mn_{0.5}O_3$ thin films can be obtained at high O_2-pressures (above 600 mTorr) and high temperatures during PLD.[2]

Van der Pauw

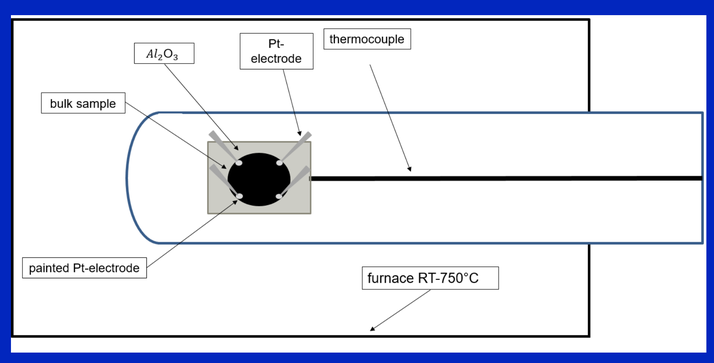

Fig.2: Van der Pauw measurement setup

Van der Pauw method is mostly used for the determination of the specific resistivity of thin, flat samples of arbitrary shape.[3]

TEM Cross-Section Images

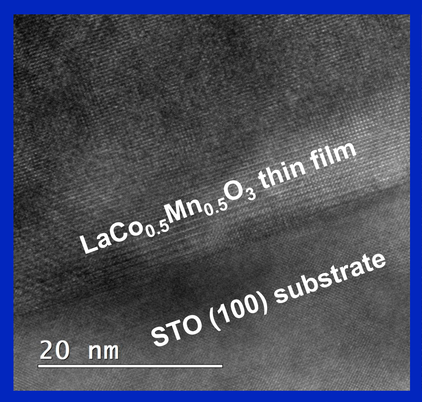

Fig.3: TEM cross-section images show single phase, epitaxially grown thin films.

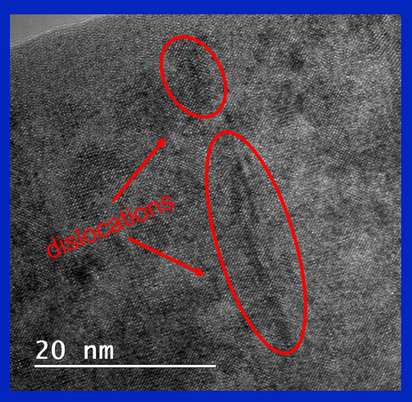

Fig.4: The higher the $p(O_2)$ during growth the more likely dislocations evolve.

AFM Measurements

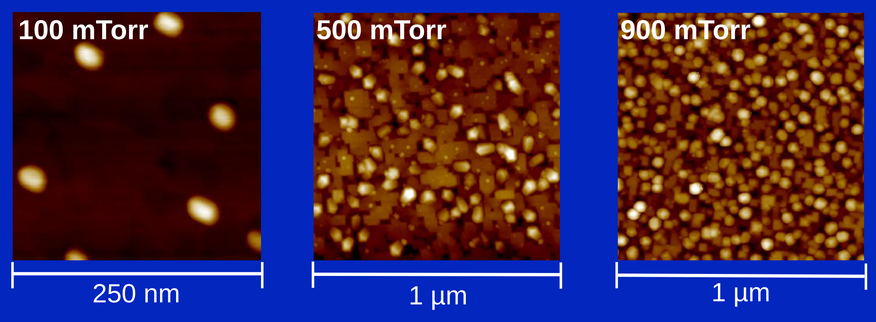

Fig.5: AFM measurements of three thin films, deposited on $LaAlO_3$ under 5 Hz and 100 mTorr, 500 mTorr or 900 mTorr oxygen background pressure.

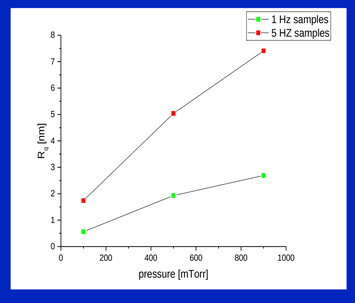

Fig.6: Root Mean Square Roughness (Rq) evolution with increasing $p(O_2)$ during PLD.

The higher the deposition frequency and the higher the $p(O_2)$ during the PLD process the rougher the surface of the thin films.

Electrical Properties

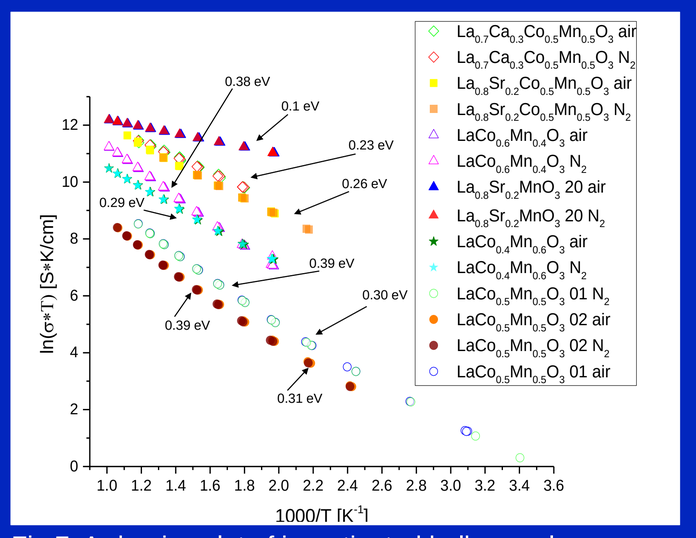

Fig.7: Arrhenius plot of investigated bulk samples.

All listed bulk samples were measured in ambient air and N_2 containing nominal 2 ppm O_2. The reducing atmosphere did not have any influence on the sample's conductivity. A-site doping enhances the conductivity.

SIMS Depth Profiles

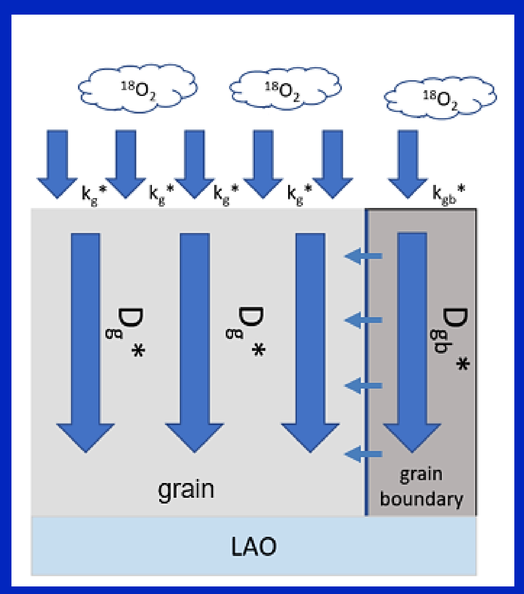

Fig.8: Diffusion model of bulk and grain boundary diffusion.

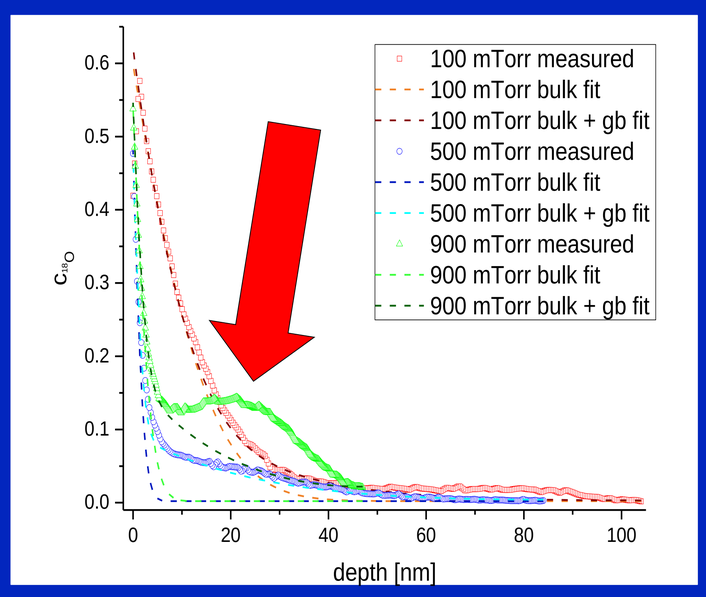

Fig.9: ^{18}O ion depth profiles of three $LaCo_{0.5}Mn_{0.5}O_3$ thin films on $LaAlO_3$, bulk and bulk + grain boundary diffusion fitting curves after a diffusion at 600 °C for 15 hours.

Tab.1: Diffusion and surface exchange coefficients of $LaCo_{0.5}Mn_{0.5}O_3$ thin films after exchange at 600 °C for 15 hours.

$p(O_2)$ in PLD [mTorr]	D*_g [m²/s]	D*_gb [m²/s]	k*_g [m/s]	k*_gb [m/s]
100	1.40E-21	7.50E-20	2.25E-13	1.00E-12
100	1.14E-21	1.65E-20	2.00E-13	2.05E-12
500	3.52E-23	2.20E-20	1.64E-14	1.38E-12
900	6.00E-23	1.65E-20	2.81E-14	8.60E-13
900	4.50E-23	1.40E-20	2.70E-14	1.09E-12

Grain boundary diffusion plays a vital role in $LaCo_{0.5}Mn_{0.5}O_3$. Consequently, considering only bulk diffusion leads to a tremendous mismatch between the fitted and the measured curve. A change in the shape of the ^{18}O ion depth profiles based on an increased oxygen background pressure during the pulsed laser deposition indicates an additional diffusion process. This is most probably related to an enhanced dislocation concentration.

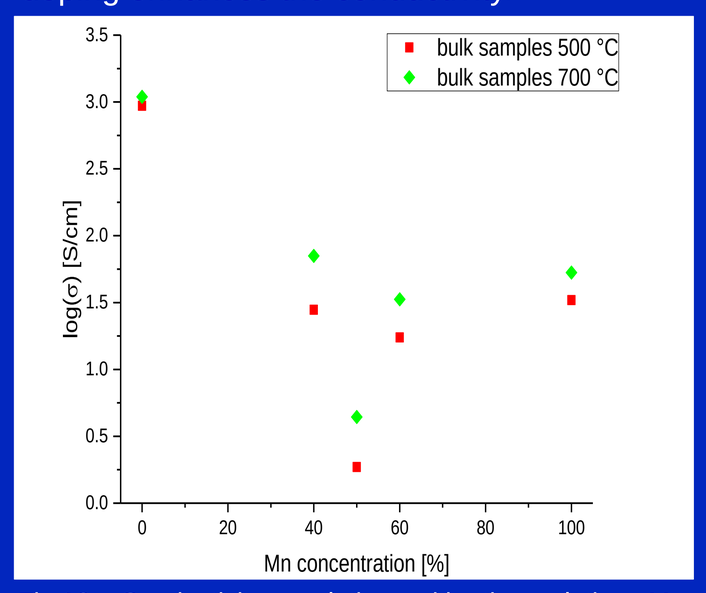

Fig.10: Conductivity evolution with the relative Mn concentration.

In undoped $LaCo_{1-x}Mn_xO_3$ bulk samples conductivity changes with the ratio between Co and Mn. $LaCoO_3$ exhibits by far the highest conductivity, it is in a range of 1000 S/cm and temperature seems to have a minor impact[4]. By increasing the Mn concentration the conductivity drops sharply to 28 S/cm at 500 °C respectively 71 S/cm at 700 °C for 40 % Mn. The maximum of the measured resistivity is reached at a Mn concentration of 50 %. A further increase of the relative amount of Mn causes an other rise in conductivity.

Acknowledgements

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Conclusion

- Oxygen diffuses mostly through fast grain boundaries
- Worst conductivity at a Co:Mn ratio of 1:1
- A-site doping with Ca or Sr (p-type) increases conductivity tremendously

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