

Short-Term and Long-Term Chemical Expansion
Effects in the Mixed-Conductor $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$

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We have measured the thermal and chemical expansion properties of polycrystalline $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ (LSC) ($x = 0.2, 0.4, \text{ and } 0.7$) at $600^\circ\text{C} < T < 900^\circ\text{C}$ and $10^{-4} \text{ atm} < P_{\text{O}_2} < 1 \text{ atm}$ using controlled-atmosphere dilatometry. The thermal expansivity, β_T , was found to be nearly constant from 25 to 900°C , indicating that increases observed in the coefficient of thermal expansion (CTE) at high temperature and constant P_{O_2} is caused primarily by changes in cobalt oxidation state and/or structure. This “chemical” expansion was found to involve two components: a larger, rapidly-equilibrating component associated with short-term changes in oxygen vacancy concentration, and a smaller, slowly-equilibrating component, possibly associated with cation rearrangement following a change in average cobalt oxidation state.

Describing the faster component in terms of the oxygen vacancy chemical expansivity (β_C), we found that β_C generally increases with oxygen vacancy concentration, and can be expressed on a universal curve encompassing data at all temperatures, P_{O_2} 's and Sr contents (Fig. 1). Possible reasons for the observed nonlinearity are discussed, and compared to other materials of both similar and different structure types.

The much smaller, slowly-equilibrating component of expansion appears as a nearly linear variation in strain with time at constant T and P_{O_2} , following a change in P_{O_2} . The direction of strain variation was found to be a function of P_{O_2} , and this effect is much more pronounced in $\text{La}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ than in LSC with $x = 0.2$ or 0.4 . Possible explanations for this behavior are discussed in terms of microdomains (nanostructure) and slow changes in cation ordering near a phase transition.

We have also used transient expansion measurements to quantify oxygen chemical diffusion and surface exchange in the LSC system. Preliminary results of these measurements will be presented.

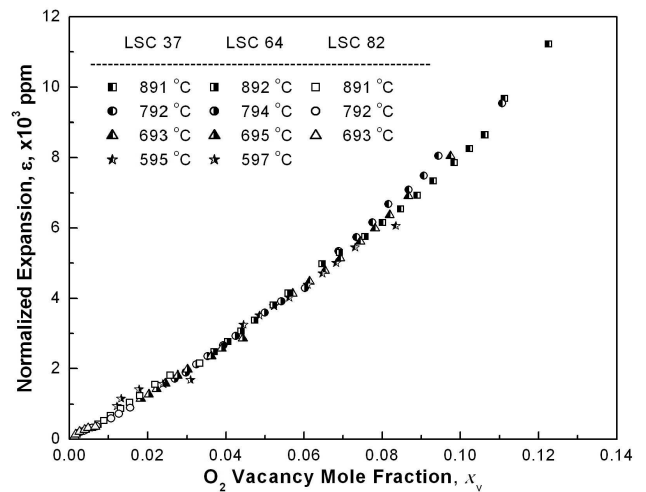


Fig. 1. Chemical expansion of LSC, obtained by subtracting thermal expansion from the total expansion. Data shown include materials having $x = 0.2, 0.4, \text{ and } 0.7$, temperatures from $600\text{--}900^\circ\text{C}$, and P_{O_2} 's from 10^{-4} to 1 atm.

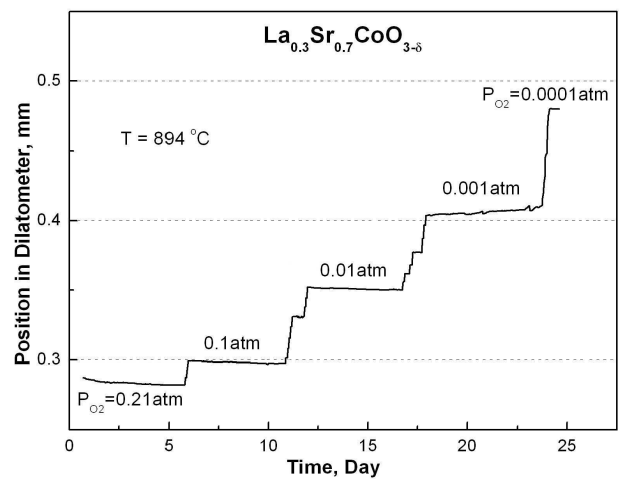


Fig. 2. Raw expansion trace of LSC ($x=0.7$) at constant temperature. The vertical step changes in expansion result from relatively rapid equilibration of oxygen content following a change in P_{O_2} . Note slow variation of expansion over a period of ~ 5 days following each P_{O_2} step. Such variations are reproducible, and absent in blank studies of alumina.