



Experiment title:

**Charge Ordering in Mixed Valence Rare Earth
Sr-doped Cobaltates**

Experiment

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HE-1849

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ID31

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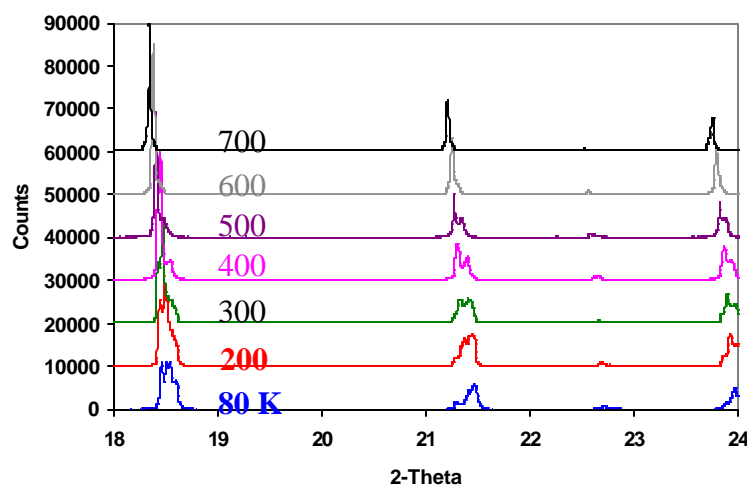
Report:

Structural Evolution in $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$ Perovskites

We have examined the structural evolution in $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-d}$ perovskites as a function of Sr-doping and temperature. Preliminary structural analysis of data collected at 298 K, reveals three distinct phases: $0 \leq x \leq 0.4$: orthorhombic $Pnma$ ($\sqrt{2}a_p \times 2a_p \times \sqrt{2}a_p$; where “ a_p ” is the dimensions of the basic perovskite unit); $0.5 \leq x \leq 0.7$: a biphasic region; and a simple cubic ($Pm-3m$) phase for $0.8 \leq x \leq 0.9$.

The structural evolution of the “biphasic” composition $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-\delta}$ as a function of temperature between 80 K and 750 K reveals that a single (simple cubic $Pm-3m$) phase is present above 600K (Figure 1).

Figure 1. Evolution of the “biphasic” $\text{Nd}_{0.4}\text{Sr}_{0.6}\text{CoO}_{3-d}$ with temperature



Structural variation in the $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ family of compounds.

The $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ family of compounds forms single phase samples for compositions $x > 0.6$. Our previous studies indicated that for $0.6 < x \leq 0.9$, a $2a_p \times 2a_p \times 4a_p$ tetragonal ($I4/mmm$) superstructure is formed; while the $x = 0.95$ composition crystallises with a $a_p \times a_p \times 2a_p$ tetragonal ($P4/mmm$) superstructure at 295 K.

We collected diffraction patterns for $\text{Ho}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ for $x = 0.7, 0.8$, and 0.9 at temperatures ranging from 80 K to 700 K. At room temperature, $\text{Ho}_{0.30}\text{Sr}_{0.70}\text{CoO}_{3-\delta}$ and $\text{Ho}_{0.10}\text{Sr}_{0.90}\text{CoO}_{3-\delta}$ showed tetragonal ($I4/mmm$: $2a_p \times 2a_p \times 4a_p$) perovskite superstructures. Data for $\text{Ho}_{0.20}\text{Sr}_{0.80}\text{CoO}_{3-\delta}$ showed an additional structural modulation, leading to a larger orthorhombic ($Amam$: $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$) cell (see below).

Both samples of $\text{Ho}_{0.3}\text{Sr}_{0.7}\text{CoO}_{3-\delta}$ and $\text{Ho}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ showed structural transitions as a function of temperature. $\text{Ho}_{0.1}\text{Sr}_{0.9}\text{CoO}_{3-\delta}$ showed only thermal expansion with increasing temperature.

Structural Modulations in $\text{Ln}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ ($\text{Ln} = \text{Dy}^{3+}, \text{Ho}^{3+}, \text{Er}^{3+}$ and Tm^{3+}) Perovskites

During experiment HE-1716, we noted additional splittings and superstructure reflections associated with the composition $\text{Y}_{0.20}\text{Sr}_{0.80}\text{CoO}_{3-\delta}$. At odds with the structure reported in the literature for this composition (tetragonal, $I4/mmm$: $2a_p \times 2a_p \times 4a_p$), we determined the cell to be a larger orthorhombic structure.

We measured the diffraction profiles for $\text{Ln}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($\text{Ln} = \text{Gd-Tm}$; $x = 0.8$) at room temperature and observed an additional structural modulation associated with Ln/Sr and $\text{O}/\text{vacancy}$ ordering for $\text{Ln} = \text{Dy-Tm}$. As in the case of $\text{Ho}_{0.20}\text{Sr}_{0.80}\text{CoO}_{3-\delta}$, structures have been able to be indexed using the orthorhombic ($Amam$: $4\sqrt{2}a_p \times 2\sqrt{2}a_p \times 4a_p$) cell. The additional contrast between the rare earth ions (Ln^{3+}) and Sr^{2+} (compared to isoelectronic Y^{3+} and Sr^{2+} used in our previous experiment) enabled us to successfully index this phase.

Examination of $\text{Tm}_{0.20}\text{Sr}_{0.80}\text{CoO}_{3-\delta}$, as a function of temperature revealed an intermediate phase between room temperature and the high temperature tetragonal (Figure 2).

Structure solution and refinements for each of these phases is continuing.

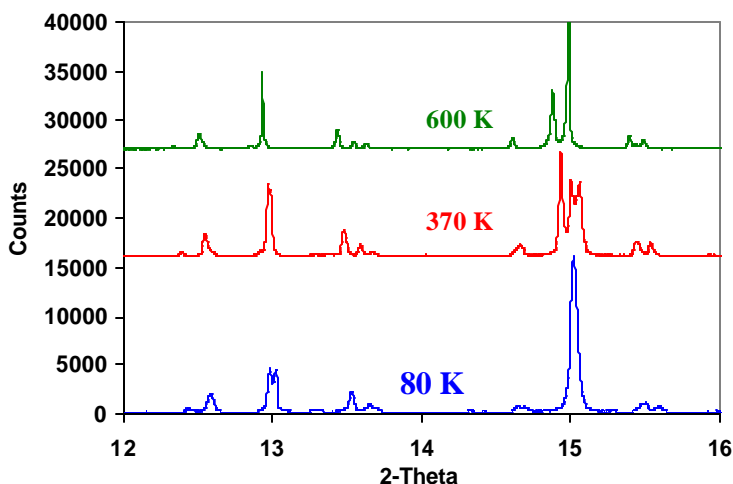


Figure 2. Diffraction data for orthorhombic, intermediate and tetragonal phases for $\text{Tm}_{0.2}\text{Sr}_{0.8}\text{CoO}_{3-\delta}$ at 80 K, 370 K and 600 K respectively.