Crystal structure and oxygen nonstoichiometry of the $Ho_xSr_{1-x}CoO_{3-\delta}$

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Samples with overall composition $Ho_xSr_{1-x}CoO_{3-\delta}$ within the range $0.05 \le x \le 0.9$ were prepared by a solid-state technique at 1100 °C in air. Single-phase $Ho_xSr_{1-x}CoO_{3-\delta}$ oxides were obtained within the range $0.05 \le x \le 0.30$. Solid solutions of $Ho_{0.05}Sr_{0.95}CoO_{3-\delta}$ and $Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$ were indexed in the cubic structure (*Pm3m* sp. gr.) with the unit cell parameters $a = 3.846$ Å and $a = 3.842$ Å, respectively. Further introduction of holmium leads to a change of crystal structure from cubic to a tetragonal $2a_p \times 2a_p \times 4a_p$ superstructure. All samples with $x > 0.3$ were multiphase, containing a saturated solid solution with approximate composition $Ho_{0.3}Sr_{0.7}CoO_{3-\delta}$ with Ho_2O_3 and CoO. The change of oxygen nonstoichiometry was measured by thermogravimetric analysis within the temperature range $25 \le T$ (°C) ≤ 1100. The absolute value of oxygen nonstoichiometry was calculated from the results of chromatometric titration. Thermal expansion coefficients of $Ho_{1-x}Sr_xCoO_{3-\delta}$ were measured by dilatometry within the temperature range $25 \le T$ (°C) ≤ 1100 in air.

I. INTRODUCTION

The family of mixed rare earth and alkali earth cobaltates $Ln_{1-x}Sr_xCoO_{3-\delta}$ attract significant attention as promising electrode materials for different electrochemical applications, such as cathode materials for solid oxide fuel cells, oxygen separation membranes.[1] All these applications require detailed description and analysis of synthesis methods, crystal structure, phase equilibria, and other properties. Important functional properties, e.g., electrical conductivity, ion mobility, chemical expansion, strongly depend on oxygen nonstoichiometry. Such kind of studies, performed in detail for Ln = La–Sm,[2] still lack for heavier rare earth containing systems, such as Ho.

Holmium cobaltate $HoCoO_{3-\delta}$ can be prepared, e.g., by sol–gel[3] or solid-state reaction[4,5] in air or at high oxygen pressure[6] and possesses an orthorhombically distorted perovskite structure with unit cell parameters: $a = 5.147(2)$, $b = 5.417(2)$, and $c = 7.375(3)$ Å.[6]

Thermodynamic stability of $HoCoO_{3-\delta}$ in air is limited to 1050 °C,[5] and above this temperature, it decomposes according to the reaction:

$$HoCoO_{3-\delta} = \frac{1}{2} Ho_2O_3 + CoO + (0.5 - \delta)/2\, O_2 \quad . \quad (1)$$

However, the decomposition temperature of $HoCoO_{3-\delta}$ in air evaluated from the results reported in Ref. 3 is approximately 1124 °C, which is higher than the temperature mentioned above[5] and also contradictory to the synthesis temperature 1150 °C used in the latter work.[3]

Within the general formula of $SrCoO_{3-\delta}$, a number of oxides with different structures formed in air depending on temperature or oxygen content ($2.29 \le 3-\delta \le 2.80$).[7] At temperatures around 1100 °C in air, a rhombohedral brownmillerite type structure (usually written as $Sr_2Co_2O_{5 \pm y}$) with oxygen content $2.42 < 3-\delta < 2.52$ is formed.[8,9] An increase of oxygen partial pressure (1–10^3 atm) led to the formation of cubic $SrCoO_{3-\delta}$ with $2.67 < 3-\delta < 3.00$.[10]

Precise study of crystal structure of mixed holmium strontium cobaltates $Ho_xSr_{1-x}CoO_{3-\delta}$ and ordering effects of cations in A-position and oxygen vacancy ordering have been performed recently.[11–13] Although the influence of oxygen nonstoichiometry on crystal structure and properties were shown elsewhere,[11–14] a systematic study of oxygen content versus temperature has not been performed yet. Only oxygen nonstoichiometries for some samples with the certain composition obtained at different conditions were determined. Information concerning the values of substitution limits reported by different authors also differs. For example, Istomin et al.[12] reported a homogeneity range of $0 < x \le 0.3$, whereas Chiang et al.[15] studied samples with $x = 0.45$ and 0.55.

In the present study, the homogeneity range of $Ho_xSr_{1-x}CoO_{3-\delta}$ was studied at 1100 °C in air; oxygen nonstoichiometry and thermal expansion behavior versus temperature $25 \le T$ °C ≤ 1100 in air were measured.

II. EXPERIMENTAL

Polycrystalline samples of $Ho_xSr_{1-x}CoO_{3-\delta}$ were synthesized by a solid-state reaction using Ho_2O_3, $SrCO_3$,

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and Co_3O_4 as starting materials. The stoichiometric mixtures of oxides and strontium carbonate were ground in an agate mortar. Two primary anneals were performed at 800 and 900 °C, and then, the samples were fired at 1100 °C for 120 h in air with intermediate grindings and slowly cooled to room temperature at the rate of about 100 °C/h.

Phase identification was performed by x-ray diffraction (XRD) analysis using a DRON-6,0 diffractometer with CuK_α radiation. Unit cell parameters were refined using the Fullprof package. For high temperature XRD measurements (25–530 °C), a DRON-6,0 diffractometer was equipped with the special attachment HDK S1 (Edmund Buehler GmbH, Hechingen, Germany).

The change of oxygen nonstoichiometry was measured by thermogravimetric (TG) analysis within the temperature range $25 \leq T$ (°C) ≤ 1100 in air using Simultaneous Thermal Analyzer STA 409 PC (Netzsch Gmbh, Selb, Germany). The measurements were performed in static conditions (8–10 h step at constant temperature).

The absolute value of oxygen nonstoichiometry was calculated from the electroneutrality condition for nonstoichiometric holmium strontium cobaltates $Ho_xSr_{1-x}CoO_{3-\delta}$ slowly cooled to room temperature. The mean oxidation state of cobalt ions was measured by chromatometric titration. The sample (~0.2 g) was dissolved in 2 M hydrochloric acid in the presence of a known amount of Mohr salt Fe $(NH_4)_2(SO_4)_2 \times 6H_2O$ taken in excess. The amount of Fe^{2+} ions, left after reaction (2) was completed, were then titrated by 0.1 N solution of potassium dichromate (reaction 3):

$$(n-2)Fe^{2+} + Co^{n+} \leftrightarrow (n-2)Fe^{3+} + Co^{2+} \quad , \quad (2)$$

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \leftrightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O \quad . \quad (3)$$

The equivalent point was registered with the help of the automatic titrator, Akvilon ATP-02 (St. Petersburg, Russia).

Thermal expansion coefficients (TECs) of $Ho_{1-x}Sr_xCoO_{3-\delta}$ were measured using a Netzsch DIL 402C dilatometer within the temperature range $25 \leq T$ (°C) ≤ 1100 in air. Bar-shaped samples ($4 \times 4 \times 25$ mm) for TEC measurements were obtained by pressing the powders mixed with 2–3 drops of polyvinyl alcohol water solution (10 wt%) using a manually operated press followed by sintering under slow heating conditions, holding at 1200 °C for 14 h, and slow cooling (the rate of heating and cooling was 80 K/h).

III. RESULTS AND DISCUSSION

Samples with overall composition $Ho_xSr_{1-x}CoO_{3-\delta}$ within the range $0.05 \leq x \leq 0.4$ with steps in x of 0.05 and within the range $0.4 \leq x \leq 0.9$ with steps in x of 0.1 were treated according to the ceramic technique described in the Sec. II at 1100 °C. It was found that single-phase $Ho_xSr_{1-x}CoO_{3-\delta}$ samples were obtained within the range $0.05 \leq x \leq 0.30$. Solid solution $Ho_{0.05}Sr_{0.95}CoO_{3-\delta}$ and $Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$ were indexed in the cubic structure (*Pm3m* sp. gr.) with the unit cell parameters $a = 3.846$ Å ($x = 0.05$) and $a = 3.842$ Å ($x = 0.1$), in good agreement with those reported in Ref. 12. The XRD pattern for $Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$ is shown in Fig. 1, as an example.

Further introduction of holmium leads to a change of crystal structure from cubic to tetragonal. Earlier,[11–13] it was shown that $Ho_xSr_{1-x}CoO_{3-\delta}$ forms a $2a_p \times 2a_p \times 4a_p$ superstructure as the result of a combination of A-site cation and oxygen vacancy ordering. Therefore, the samples within the range $0.15 \leq x \leq 0.30$ were refined in the tetragonal $2a_p \times 2a_p \times 4a_p$ superstructure. The XRD pattern for $Ho_{0.2}Sr_{0.8}CoO_{3-\delta}$ is shown in Fig. 2, as an example. The values of unit cell parameters, unit cell volumes, and refinement parameters for single-phase samples are listed in Table I.

The decrease of unit cell parameters and unit cell volume with increase of holmium content (Fig. 3) can be explained by the relative cation sizes since the ionic radius of holmium is smaller than the ionic radius of strontium ($r_{Ho^{3+}} = 1.015$ Å; $r_{Sr^{3+}} = 1.26$ Å; coordination number (CN) = VIII).[16] To illustrate the changes of unit cell parameter of all single phases (Fig. 3), those for the solid solutions with cubic structure were multiplied by 2 and 4, respectively.

All samples with $x > 0.3$ were multiphase and consisted of saturated solid solution having an approximate composition $Ho_{0.3}Sr_{0.7}CoO_{3-\delta}$, Ho_2O_3, and CoO.

Combining the results of the chromatometric titration and TG measurements, the values of oxygen content versus temperature were obtained (Fig. 4). It is easy to see that within the entire temperature range, an increase of holmium content increases the value of oxygen index $(3 - \delta)$. Such a tendency is obvious since Sr^{2+} ions are substituted by Ho^{3+}. As discussed below, it is also useful to analyze how oxidation state of cobalt varies with the changes of Ho/Sr ratio (Table II).

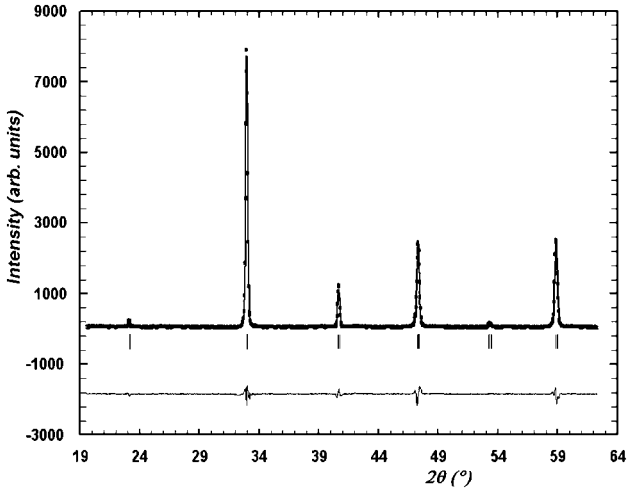


FIG. 1. XRD pattern for $Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$ refined by Rietveld analysis.

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Introduction of holmium causes oxygen to be retained more strongly in the lattice (the variation of oxygen content with the temperature is smallest for the sample with $x = 0.3$), while oxidation state of cobalt varies in a more narrow range as compared to lower x. Since the oxidation states of strontium, holmium, and oxygen ions are considered to be unchanged, the formula of solid solution can be written as follows: $Ho_x^{3+}Sr_{1-x}^{2+}Co^nO_{3-\delta}$, where n means oxidation state of cobalt ions. Thus, electroneutrality equation can be represented as:

$$3 \times x + 2 \times (1 - x) + n = 2 \times (3 - \delta) \quad . \quad (4)$$

One can easily transform the above equation to the following form:

$$n = 2 \times (3 - \delta) - 2 - x \quad . \quad (5)$$

According to the Eq. (5), oxygen content and holmium content influence the value of mean oxidation state of cobalt in opposite directions. Obtained results (Table II) show that the values of holmium content (x) and mean oxidation state of cobalt ions (n) change in the same direction at 1100 °C. These lead to the conclusion that an increase of mean oxidation state of cobalt ions (n) with the increase of holmium content (x) is caused by higher rate of oxygen content gain in comparison to (x).

An increase of Ho/Sr ratio leads to a decrease of the mean radii of cations in A-positions, whereas oxidation state of cobalt ions (at 1100 °C) increases, and therefore, ionic radius of cobalt ions (in B-position) increases. Hereby, increase of holmium content leads to the decrease of r_A/r_B ratio that reduces the stability of the perovskite structure. These are in good agreement with the fact of instability of $Ho_xSr_{1-x}CoO_{3-\delta}$ ($x > 0.3$) at 1100 °C.

Relative densities of the samples for thermal expansion measurements were evaluated by comparison of measured values to those calculated from XRD data. Obtained values of relative densities of $Ho_xSr_{1-x}CoO_{3-\delta}$ were 86% for $x = 0.1$, 87% for $x = 0.2$, and 78% for $x = 0.3$. The thermal expansion behavior of $Ho_xSr_{1-x}CoO_{3-\delta}$ ceramics was reproducible while heating and cooling (Fig. 5). Peculiar character of dependency for the sample with

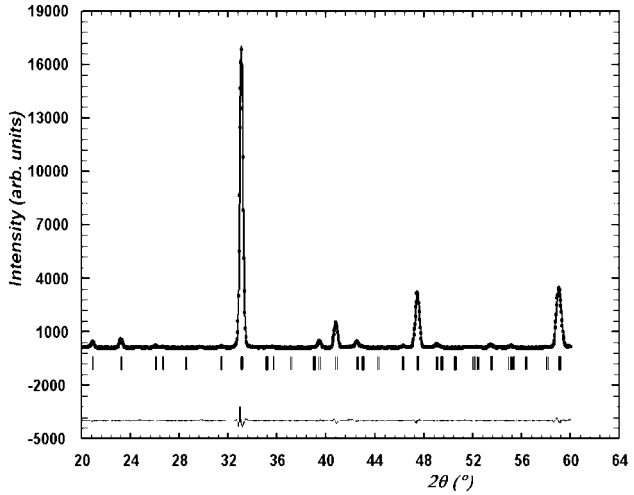


FIG. 2. XRD pattern for $Ho_{0.2}Sr_{0.8}CoO_{3-\delta}$ refined by Rietveld analysis.

TABLE I. Unit cell parameters of the $Ho_xSr_{1-x}CoO_{3-\delta}$ ($0.05 \leq x \leq 0.30$).

Composition	a, Å	b, Å	c, Å	V, (Å)^3	R_{Br}	R_f
$Ho_{0.05}Sr_{0.95}CoO_{3-\delta}$	3.846 (1)	...	...	56,89 (1)	0.78	0.53
$Ho_{0.1}Sr_{0.9}CoO_{3-\delta}$	3.842 (1)	...	...	56,70 (1)	1.71	1.48
$Ho_{0.15}Sr_{0.85}CoO_{3-\delta}$	7.668 (1)	7.668 (1)	15.362 (1)	903,25 (1)	1.08	1.64
$Ho_{0.2}Sr_{0.8}CoO_{3-\delta}$	7.654 (1)	7.654 (1)	15.333 (1)	898,28 (1)	0.37	0.66
$Ho_{0.25}Sr_{0.75}CoO_{3-\delta}$	7.634 (1)	7.634 (1)	15.311 (1)	892,29 (1)	0.78	0.70
$Ho_{0.3}Sr_{0.7}CoO_{3-\delta}$	7.623 (1)	7.623 (1)	15.309 (1)	889,53 (1)	0.89	1.12

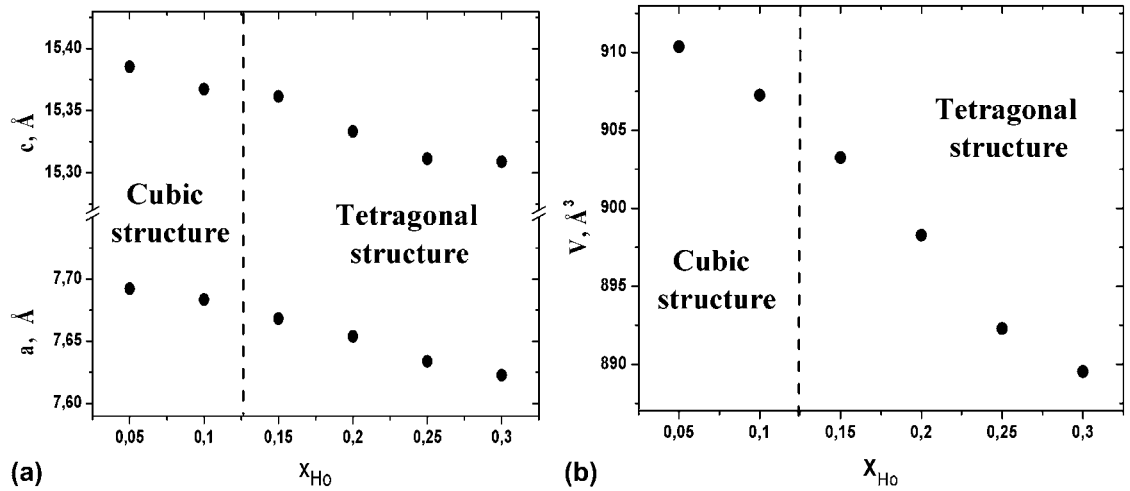


FIG. 3. The unit cell parameters *(a)* and unit cell volume *(b)* versus holmium content in $Ho_xSr_{1-x}CoO_{3-\delta}$. The unit cell parameter of the solid solutions with cubic structure ($x = 0.05$ and 0.1) was multiplied by 2 (parameters a and b) and 4 (parameter c).

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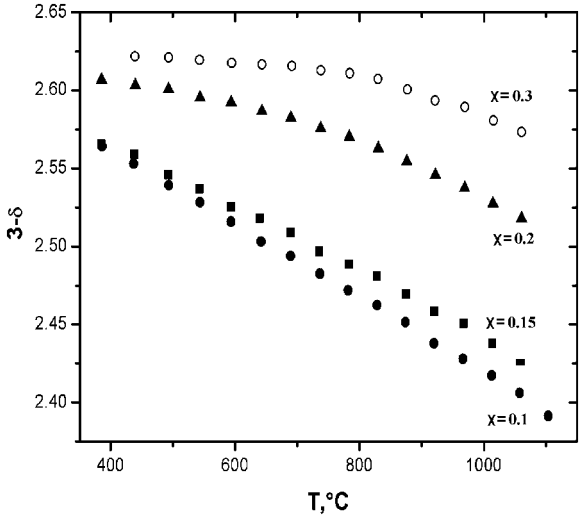


FIG. 4. Oxygen content in $Ho_xSr_{1-x}CoO_{3-\delta}$ as a function of temperature in air.

TABLE II. Mean oxidation state of cobalt ions in the $Ho_xSr_{1-x}CoO_{3-\delta}$.

T, °C	$x = 0.1$	$x = 0.15$	$x = 0.2$	$x = 0.3$
25	3.01	2.99	3.00	2.94
1100	2.68	2.70	2.84	2.85

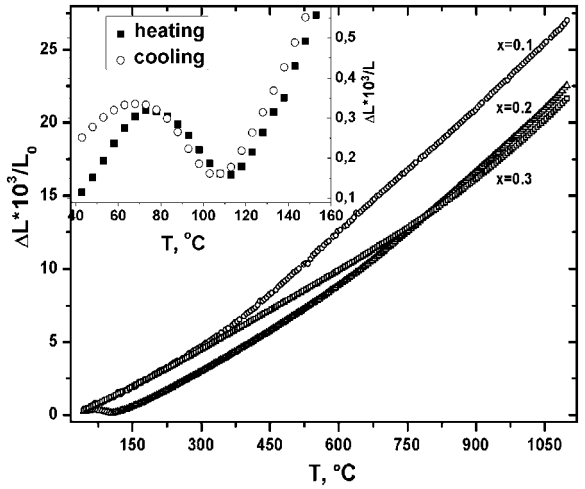


FIG. 5. Thermal expansion ($\Delta L/L_0$) for $Ho_xSr_{1-x}CoO_{3-\delta}$ in air.

$x = 0.2$ in the temperature range 25–110 °C (Fig. 5, inset) stimulated us to check the possibility of phase transition. Therefore, high temperature XRD measurements were performed for this sample. Figure 6 illustrates no visible phase transition within the studied temperature range. Thus, either such behavior corresponds to some other effects or the type of transformation cannot be detected by XRD technique, for instance, if it takes place due to oxygen order–disorder processes. The latter is unlikely since the temperature is too low. Table III lists the TECs calculated from the

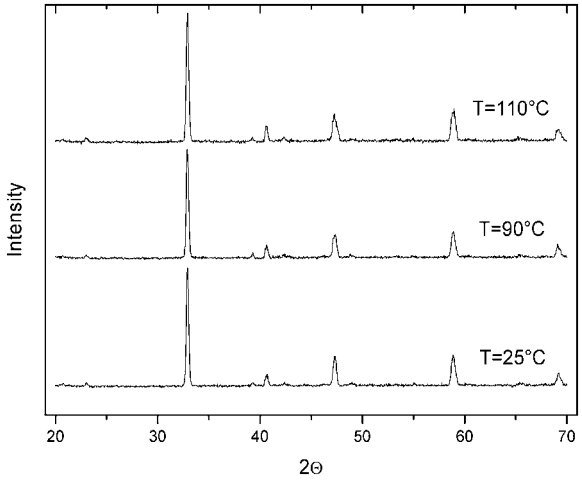


FIG. 6. XRD pattern for $Ho_{0.2}Sr_{0.8}CoO_{3-\delta}$ at different temperatures.

TABLE III. Average values of TECs of $Ho_xSr_{1-x}CoO_{3-\delta}$ within the temperature range 530–900 °C.

x	TEC $\times 10^6$ K^{-1}
0.1	28.1
0.2	25.5
0.3	20.2

dilatometric data and averaged in the temperature range 530–900 °C.

The decrease of average values of TEC with the increase of holmium content is probably related to the reduction of the unit cell volume and diminishing of oxygen exchange. It is worth to mention that thermal expansion consists of two constituents—one associated with atomic vibrations and the other related to changes in the chemical composition. The latter is known as "chemical expansion."[17]

IV. CONCLUSION

It was shown that the homogeneity range of solid solutions of $Ho_xSr_{1-x}CoO_{3-\delta}$ is $0.05 \leq x \leq 0.3$ in air at 1100 °C. An increase of holmium content leads to the transformation of $Ho_xSr_{1-x}CoO_{3-\delta}$ from a cubic to tetragonal structure. Oxygen content and thermal expansion of the $Ho_xSr_{1-x}CoO_{3-\delta}$ were also measured as a function of temperature in air.

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