

HIGH-PRESSURE DIFFRACTION STUDY OF SrCoO_{2.88} AND La_{0.33}Sr_{0.67}CoO_{2.85}

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Introduction

The Ln_{1-x}Sr_xCoO_{3-δ} solid solution oxides crystallise in perovskite-type ABO₃ structures with a lanthanide ion (*e.g.* La³⁺) or an alkaline earth ion (*e.g.* Sr²⁺) at the A site and with a cobalt ion at the B site. These oxides are subject of many studies because of their unique physical properties. It was recently shown that the presence of oxygen vacancies changes the valence state of Co ion. The oxygen content may thus influence the structural, electrical and magnetic properties of these materials. A distinctive feature that results from the oxygen deficiency is so-called mixed conductivity. This phenomenon is based on a combination of high ionic conductivity and high electronic conductivity [1]. It opens possibilities for practical applications of these materials as high temperature ceramic membranes [2] and as cathode materials for solid oxide fuels [3-5].

Ln_{1-x}Sr_xCoO_{3-δ} undergoes phase transitions which are dependent on the kind and substitution amount of the lanthanide ion [6,7]. At ambient conditions, the compound La_{1-x}Sr_xCoO_{3-δ} crystallises in *R-3c* space group up to *x* = 0.5, and *Pm-3m* for *x* from 0.6 to 0.8 [8]. The crystal structure may depend on the oxygen content. James *et al.* [6,7] have detected, using electron and neutron diffraction techniques, that the samples with *x* = 0.6 and 0.8 exhibit a weak oxygen-vacancy-based tetragonal (*I4mmm*) superstructure with doubled *c* parameter. Recently it has been shown that for highly Sr-substituted La_{0.33}Sr_{0.67}CoO_{3-δ} with oxygen vacancies (0 < δ < 0.5) three structure types are observed depending on the δ value [9].

There exist only few studies on magnetic properties of lanthanide strontium cobalt oxides under pressure (*e.g.* [10,11,13]). The structural behaviour under pressure has been studied for La_{0.82}Sr_{0.18}CoO₃, only [13]. In this study, the pressure dependence of lattice parameters is determined *in situ* by X-ray diffraction at a high-pressure (HP) dedicated synchrotron beamline for oxygen deficient samples of SrCoO_{2.88} and La_{0.33}Sr_{0.67}CoO_{2.85}.

Experimental

Phase analysis was performed using a laboratory X'Pert PRO MPD powder diffractometer. The HP studies were

carried out at F2.1 beamline (HASYLAB/DESY) using a cubic anvil X-ray diffraction press MAX80. Measurements were done using the energy-dispersive (EDXRD) mode. The diffraction angle was fixed at 4.508°. NaCl was used as pressure transmitting medium (NaCl to sample volume ratio was 5:1) and its 002 line served as a pressure calibrant. The diffraction measurements were carried out in the pressure interval of 0-43.2 kbar at 30(±2)°C. 111 diffraction peak was used for determination of the lattice parameter, as other ones overlap with NaCl peaks for the highest pressures. The bulk moduli (*K*₀) were determined by fitting the second order Birch-Murnaghan equation of state (with *K'* fixed at 4) to the experimental data, using the EOS program [12].

Results and discussion

Phase analysis indicates a simple cubic perovskite cell for La_{0.33}Sr_{0.67}CoO_{2.85}. For SrCoO_{2.88} a small distortion is possible as indicated by a slight splitting of the cubic 002 and 310 peaks; moreover, some weak peaks (height < 1.2%) belonging to secondary phases are present. X-ray diffraction spectra (shown for eight selected pressures in Figure 1) indicate no structural phase transition in the studied pressure range.

The unit cell volumes as a function of pressure determined from diffraction data are presented in Figure 2. Experimental points were fitted to the Birch-Murnaghan equation of state in the range of 0 - 23 kbar for SrCoO_{2.88} and 0 - 38 kbar for La_{0.33}Sr_{0.67}CoO_{2.85}. Some deviations from the model observed above 23 kbar for the former sample and near 5-7 kbar for the latter are thought to non-fully hydrostatic conditions inside the press. Other reasons such as a change of the structure under pressure cannot be fully excluded. The discrepancies observed for the highest pressures studied may be also influenced by inaccuracies in deconvoluting of the 111 oxide peak and 100 peak of hBN (hexagonal boron nitride, the sample-container material).

The fitting results show that La_{0.33}Sr_{0.67}CoO_{2.85} is much less compressible than SrCoO_{2.88} (*K*₀=1540(25) and 790(15) kbar, respectively; *cf.* Fig. 2). This finding correlates with recent results of magnetic measurements [11] showing that the phase-transition temperature *T*_c varies faster with pressure for SrCoO_{2.88} (*i.e.* the value of *dT*_c/*dP* is higher). Com-

parison with literature data indicates a more general trend: a partial or full replacing of Sr atoms by La atoms results in a considerable increase of K_0 . The bulk modulus for our $\text{La}_{0.33}\text{Sr}_{0.67}\text{CoO}_{2.85}$ sample is virtually identical to that for rhombohedral La-rich samples in this system determined by other groups using the diamond-anvil cell technique, namely for $\text{La}_{0.82}\text{Sr}_{0.18}\text{CoO}_3$ and LaCoO_3 ($K_0=1580(80)$ kbar [13], and 1500(20) kbar [14], respectively). Neglecting the possible influence of the oxygen nonstoichiometry and some structural differences, it seems that the bulk modulus does not vary in a broad range of Sr:La ratio. However, the most recent experiments (performed with a different pressure marker) yield a relatively low value for LaCoO_3 , $K_0=1220(30)$ kbar [15]. Therefore, the influence of composition on bulk modulus in this system requires more detailed studies.

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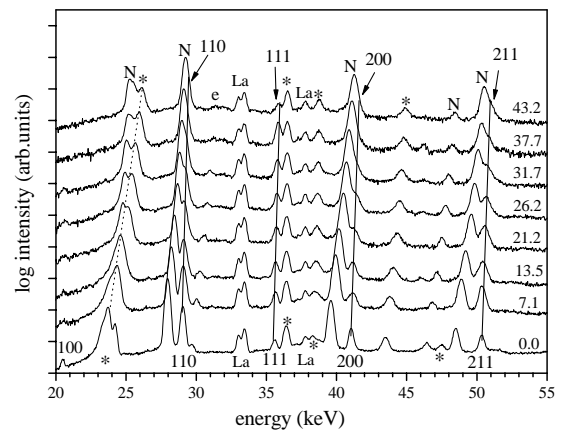
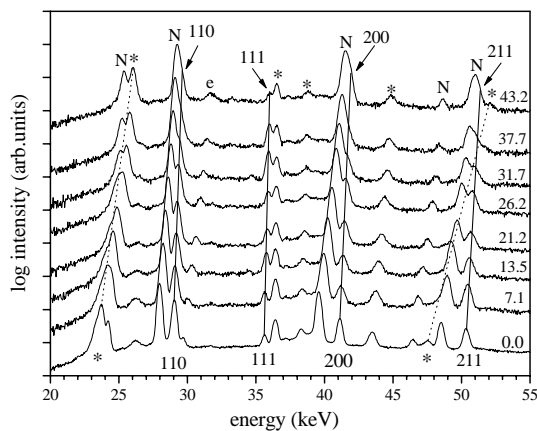


Figure 1. X-ray diffraction patterns under pressure for $\text{SrCoO}_{2.88}$ (upper left panel) and $\text{La}_{0.33}\text{Sr}_{0.67}\text{CoO}_{2.85}$ (upper right panel). The reflections from the oxides are indexed and connected (as a guide to eye) by solid lines. Peaks belonging to hBN (sample container) and NaCl are marked by "*" and "N", respectively. Fast changing 002 and 004 peaks of hBN are connected by dotted lines. The numbers on the right refer to the pressure values (in kbar units). "La" indicates the La fluorescence lines.

Figure 2. Variation of the relative unit-cell volume with pressure for both studied samples. The solid lines refer to fitted Birch-Murnaghan equation of state.

