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Crystal and magnetic structure of substituted lanthanum cobaltites

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Abstract

The crystal and magnetic structures of the lanthanum cobaltites $La_{0.6}Sr_{0.4}CoO_3$, $La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_3$ and $La_{0.6}Ba_{0.4}Co_{0.9}Fe_{0.1}O_3$ have been studied by neutron powder diffraction at temperatures of 2, 300 and 900 K. All compounds undergo a phase transition from cubic to rhombohedral structure. Below the room temperature $La_{0.6}Sr_{0.4}CoO_3$ becomes ferromagnetic while for the components with 10% Fe substituted for Co, we found an antiferromagnetic order.

Keywords: Lanthanum cobaltites; Perovskites; Powder diffraction

1. Introduction

Perovskite oxides ABO_3 with composition $La_{1-x}Sr(Ba)_xCoO_3$ are of industrial interest because of their electrical, magnetic and catalytic properties. Their essential application is for electrode material in solid-oxide fuel cells and as membranes in oxygen separation processes. The aim of the present work is to establish the influence of lattice distortion caused by different ionic size of substituted atoms on crystal and magnetic structure. We present data for the A- and B-sites substituted lanthanum cobaltites $La_{0.6}Sr_{0.4}CoO_3$, $La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_3$ and $La_{0.6}Ba_{0.4}Co_{0.9}Fe_{0.1}O_3$.

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2. Experimental

The powder samples were prepared by the citrate method. The pH value of the solution was kept at about 3 ± 1; next steps were pyrolysis at 250°C and calcination at 1200°C for 8 h in air. The single-phase quality of all samples was checked by X-ray powder diffraction. No additional phases were found.

Neutron powder diffraction experiments were performed on the flat cone diffractometer E2 and on the powder diffractometer E3 at BENSC at HMI

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Berlin. Each sample was measured at temperatures 2, 300 and 900 K. On both instruments a germanium monochromator selecting a wave- length of $\lambda = 1.217$ Å (E2) and $\lambda = 1.228$ Å (E3) was used.

3. Results

The lanthanum cobaltites $La_{0.6}Sr_{0.4}CoO_3$, $La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_3$ and $La_{0.6}Ba_{0.4}Co_{0.9}Fe_{0.1}O_3$ are rhombohedral at room temperature. They undergo a phase transition to cubic structure at

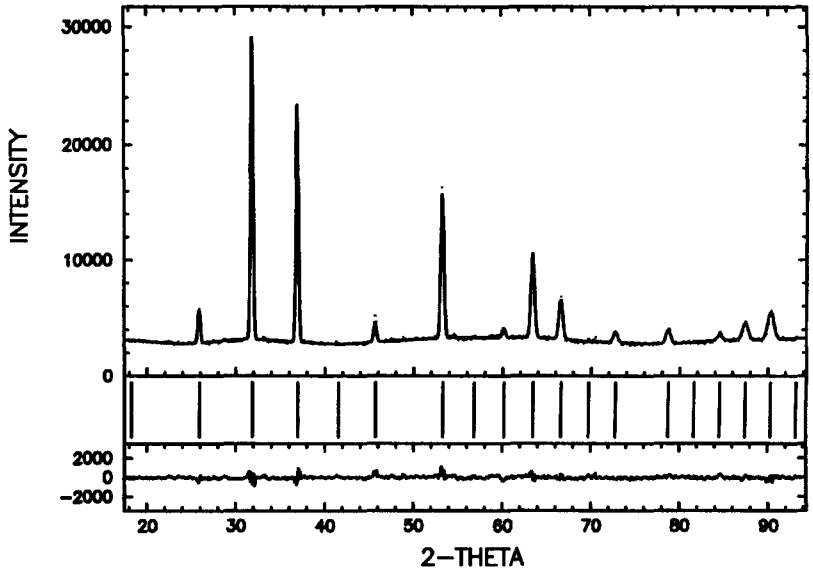

Fig. 1. Observed (circles), calculated (line) and difference plot of $La_{0.6}Sr_{0.4}CoO_3$ at $T = 900$ K.

Table 1
Lattice parameters, oxygen coordinates and agreement factors at $T = 2$, 300 and 900 K

	$La_{0.6}Sr_{0.4}CoO_3$	$La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_3$	$La_{0.6}Ba_{0.4}Co_{0.9}Fe_{0.1}O_3$
900 K (Pm3m)			
a [Å]	3.8741(3)	3.8738(3)	3.9216(4)
R_B[%]	5.6	4.6	4.4
300 K ($R\bar{3}c$)			[a]
a [Å]	5.4518(4)	5.4553(5)	5.4728(8)
c [Å]	13.257(1)	13.266(1)	13.482(3)
O (x)	0.5321(3)	0.5317(4)	0.514(1)
R_B [%]	3.9	4.6	7.4
2 K ($R\bar{3}c$)			
a [Å]	5.4159(6)	5.4210(8)	5.4810(9)
c [Å]	13.192(2)	13.148(2)	13.399(6)
O (x)	0.5290(4)	0.5334(6)	0.515(1)
R_B [%]	5.5	7.9	7.2

[a] $T = 250$ K.

temperatures around 600 K. For example, Fig. 1 shows the neutron powder diffractogram and its refinement in cubic space group Pm3m for $La_{0.6}Sr_{0.4}CoO_3$ at 900 K. La, Sr and Ba atoms occupy the 1a site (0 0 0), Co and Fe the 1b site ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) and oxygen the 3c site ($0\frac{1}{2}\frac{1}{2}$). All samples have rhombohedral symmetry at room temperature and at 2 K and were refined in space group $R\bar{3}c$. La, Sr and Ba atoms occupy the 6a site ($0\,0\,\frac{1}{4}$), Co and Fe the 6b site (0 0 0) and oxygen the 18e site ($x\,0\,\frac{1}{4}$). The lattice parameters, oxygen coordinates and agreement factors for all samples are presented in Table 1.

According to [1] pure $LaCoO_3$ is paramagnetic. The substituted $La_{1-x}Sr_xCoO_3$ becomes ferromagnetic where the transition temperature depends on

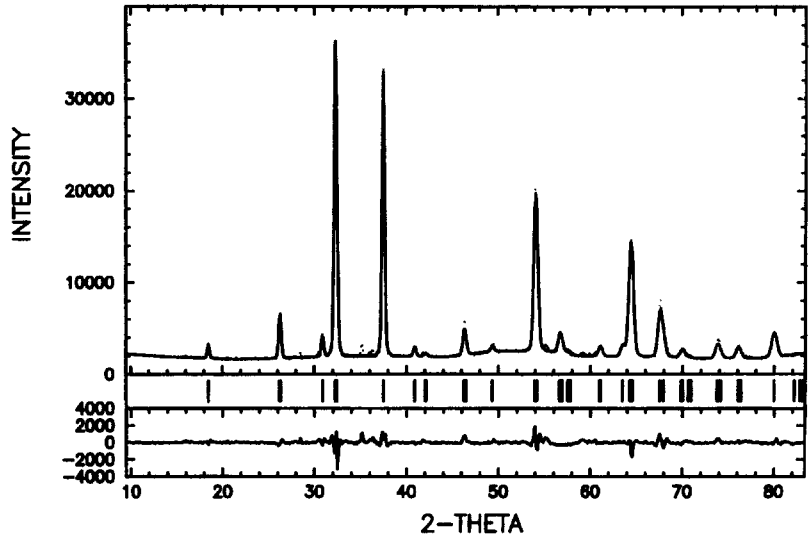

Fig. 2. Observed (circles), calculated (line) and difference plot of ferromagnetic $La_{0.6}Sr_{0.4}CoO_3$ at $T = 2$ K.

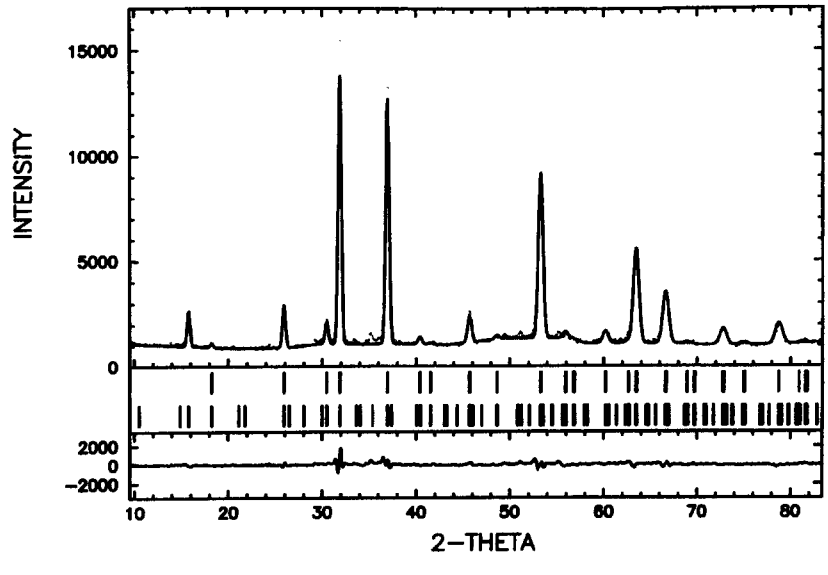

Fig. 3. Observed (circles), calculated (line) and difference plot of antiferromagnetic $La_{0.6}Ba_{0.4}Co_{0.9}Fe_{0.1}O_3$ at $T = 2$ K.

the amount of Co^{4+} ions [1–3]. Fig. 2 shows the neutron powder diffractogram of ferromagnetic $La_{0.6}Sr_{0.4}CoO_3$ at 2 K. The refined average magnetic moment per Co ion is $1.35(5)\mu_B$. The direction of the magnetic moment could not be determined from the powder data because the rhombohedral deviation from the cubic structure is small for all investigated samples.

For the B-site substituted samples an additional magnetic reflection is observed at small angle region due to antiferromagnetic ordering. The refinement for $La_{0.6}Sr_{0.4}Co_{0.9}Fe_{0.1}O_3$ at $T = 2$ K yielded an averaged magnetic moment of 1.39(8) Bohr magnetons per Co atom. The replacement of Sr atoms by larger Ba atoms now leads to an increasing of the a- and c-lattice constants as well as to an increase of the average magnetic moment per Co ion to $1.66(4)\mu_B$ at $T = 2$ K (see Fig. 3).

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