

# Neutron-diffraction and Mössbauer-spectroscopy study of $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-y}$ ( $x = 0, 0.5$ ) perovskites

S. Neov<sup>1,\*</sup>, L. Dabrowski<sup>2</sup>, M. Hofmann<sup>3</sup>, H.J.M. Bouwmeester<sup>4</sup>

<sup>1</sup>Institute for Nuclear Research and Nuclear Energy, 1784 Sofia, Bulgaria

<sup>2</sup>Institute of Atomic Energy, 05-400 Świerk, Poland

<sup>3</sup>Hahn-Meitner-Institut, BENS-NE, Glienicker Str. 100, 14109 Berlin, Germany

<sup>4</sup>University of Twente, 7500 AE Enschede, The Netherlands

Received: 18 July 2001/Accepted: 11 December 2001 – © Springer-Verlag 2002

**Abstract.** The crystal and magnetic structure of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{1-x}\text{Co}_x\text{O}_{3-y}$  ( $x = 0, 0.5$ ) perovskites was studied by neutron diffraction and Mössbauer spectroscopy. At  $T = 2\text{--}300$  K the oxides possess an oxygen-deficient, rhombohedrally distorted structure, with space group  $R\bar{3}c$ .  $^{57}\text{Fe}$  Mössbauer spectra below  $T = 154$  K show a regular arrangement of Fe spins, determined as a G-type antiferromagnetic structure by neutron diffraction. The mean magnetic moment at  $T = 40$  K is  $1.61 \mu_B$  per B-site for  $x = 0.5$ , and  $2.63 \mu_B$  for the  $x = 0$  composition. An increase of  $T_N$  and oxygen deficiency accompany the heating to 850 K. The structure of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Fe}_{0.5}\text{Co}_{0.5}\text{O}_{2.84}$  at 850 K is cubic with space group  $Pm\bar{3}m$ .

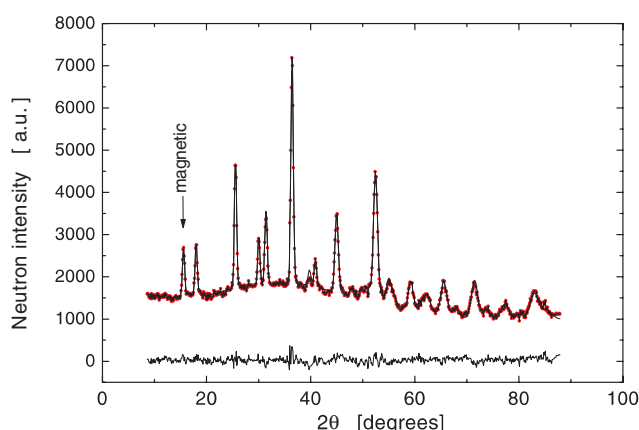
**PACS:** 61.10.-i; 61.12.-q; 75.25.+z

The interest in the structural changes of substituted lanthanum cobaltites with enhanced oxygen-transport properties is stimulated by their promising applications as oxygen-separation membranes and cathodes in solid-oxide fuel cells operating at 500–700 °C [1]. To preserve the charge neutrality of the solid solution, in mixed-valence La cobaltites the substitution of  $\text{La}^{3+}$  by  $\text{Ba}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Ca}^{2+}$  is accompanied by changes in the oxidation state of the B-site ions and formation of oxygen vacancies. This process often causes a distortion of the parent cubic lattice, thereby producing structures with different crystal symmetry, magnetic and electrical properties. In this communication, we report the results of X-ray and neutron-diffraction and Mössbauer-spectroscopy measurements on two perovskite samples in the temperature range  $T = 2\text{--}850$  K.

## 1 Experimental

Samples with composition  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$  (no. 1) and  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$  (no. 2) were prepared by the citrate

method. Metal nitrate solutions were mixed in the appropriate ratio. About 1.5 mole of citric acid per mole of metal was added and the solution was then evaporated and pyrolysed at 250 °C. The powder obtained was calcined at 1100 °C in air for 8 h. The cooling to room temperature was performed at a rate of  $0.5^\circ \text{min}^{-1}$  to ensure equilibrium with the ambient atmosphere. Sample no. 2 was heated to 850 K in vacuum during 2 h and measured again. Throughout the text the thermally treated sample is denoted as no. 3. Neutron-diffraction (ND) experiments were conducted on the BER-II reactor in BENS-NE, HMI-Berlin using two instruments: (a) E2, flat-cone diffractometer, Ge 311 monochromator,  $80^\circ$  position-sensitive detector (PSD),  $\lambda = 0.1217$  nm,  $T = 2\text{--}300$  K, Fig. 1, and (b) E6 focusing single-crystal diffractometer,  $\lambda = 0.24485$  nm,  $20^\circ$  PSD,  $T = 40\text{--}850$  K.  $^{57}\text{Fe}$  transmission-geometry Mössbauer spectroscopy (MS) data (50 mCi  $\gamma$ -source) were collected in the temperature interval 4.2–600 K.



**Fig. 1.** Neutron-diffraction spectrum, fitting curve and difference data of  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{2.86}$ ,  $\lambda = 0.1217$  nm,  $T = 2$  K

## 2 Results and discussion

The crystal and magnetic structure was determined by Rietveld analysis of diffraction data (ND and X-ray) using the

\*Corresponding author.

(Fax: +359-2/975-3619, E-mail: sneov@inrne.bas.bg)

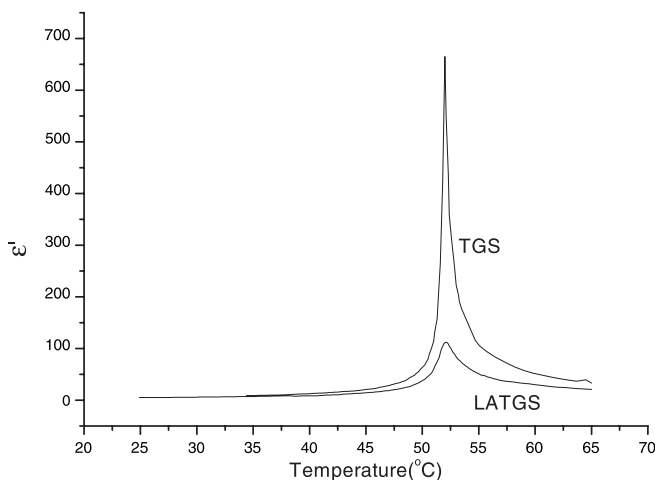
**Table 1.** Structure parameters of sample nos. 1, 2 and 3

$T$ (K)	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$\mu_{\text{B-site}}$ ( $\mu_{\text{B}}$ )	Oxygen content	Fe-O, Å/ Fe-O-Fe, deg
$\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-y}$ , sample no. 1, $\lambda = 0.1217$ nm						
2	5.52432(11)	13.4442(50)	355.3	2.63(4)	2.83(2)	1.965/165.20
300	5.53029(18)	13.4667(85)	356.7	2.15(7)	2.86(4)	1.964/167.10
$\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_{3-y}$ , sample nos. 2 and 3, $\lambda = 0.2448$ nm						
60	5.47455(21)	13.3050(15)	345.3	1.61(5)	2.90(2)	1.963/169.430
*60	5.47140(70)	13.3050(15)	344.8	1.63(5)	2.84(2)	1.938/169.620
300	5.47820(34)	13.3258(16)	346.4	0	2.92(2)	1.939/170.160
*850, cubic	3.9054(13)	3.9054(13)	59.56	0	2.84(2)	1.953/180

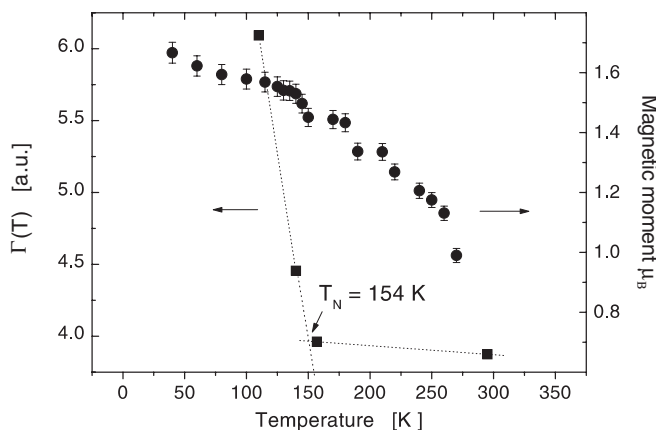
Data for sample no. 3 are indicated by \*60 and \*850.  $\text{La}^{3+}/\text{Sr}^{2+}$  are in  $6a$  (0, 0, 1/4);  $\text{Fe}^{3+}/\text{Co}^{3+}$  in  $6b$  (0, 0, 0) and  $\text{O}^{2-}$  in  $18e$  ( $x$ , 0, 1/4) Wyckoff positions. The isotropic temperature factors are  $B_{\text{La}} = 0.35(6)$ ,  $B_{\text{Fe}} = 0.63(7)$  and  $B_{\text{O}} = 1.13(7) \times 10^{-2} \text{Å}^2$ . The agreement factors are  $R_{\text{magn}} = 12.1\%$ ,  $R_{\text{Bragg}} = 6.77\%$  and  $\chi^2 = 2.72$

Fullprof program [2]. Depending on Goldschmidt's tolerance factor,  $t = (r_{\text{O}} + r_{\text{A}})/\sqrt{2}(r_{\text{B}} + r_{\text{O}})$ , where  $r_i$  are the effective radii of  $i$ -type ions, the structure of  $\text{ABO}_3$  perovskites can be cubic, orthorhombic or rhombohedral. For the studied samples the value of  $t$ ,  $t \approx 0.88$ , lies in the region between the rhombohedral and orthorhombic structures. All the observed Bragg peaks were indexed in rhombohedral space group  $R\bar{3}c$ . The crystallographic parameters obtained from the refinement are presented in Table 1. The registered rhombohedral distortion is a result of compression of the body diagonals,  $\langle 111 \rangle$  direction, relative to those in the ideal cubic perovskite structure.

In fact, by diffraction experiments on sample no. 3 at different temperatures, we observed a more than three times higher value of the linear coefficient of expansion along the  $c$  axis (hexagonal setting) in comparison with that along the  $a$  axis:  $\sigma_c = 10.5 \times 10^{-5}$ ,  $\sigma_a = 3.10 \times 10^{-5}$  (Å/K). At high temperature,  $T = 850$  K, the rhombohedral distortion of sample no. 2 is negligible and the lattice symmetry is cubic,  $Pm\bar{3}m$ . MS data indicate that at 4.2 K  $\text{FeO}_6$  octahedra remain undistorted: despite the lattice deformation the quadrupole splitting is zero. The same effect has been registered in many defective lanthanum perovskites [3–5]. The MS spectrum of sample no. 2 measured at 4.2 K, Fig. 2, is a superposition of four components of the Zeeman sextet:

**Fig. 2.** Mössbauer spectrum of sample no. 2,  $T = 4.2$  K

three hyperfine fields with flux density  $B$  of 51.6 T, 48.1 T and 45.4 T and one of 29.4 T. The observed effective magnetic fields,  $B > 45$  T, undoubtedly can be related to the high spin state of the  $\text{Fe}^{3+}$  ion in differing oxygen coordination and cation surroundings [4, 5]. The fourth component ( $B = 29.4$  T) can be attributed to the tetravalent  $\text{Fe}^{4+}$  or pentavalent  $\text{Fe}^{5+}$  state [4, 5]. From the experimental data, sample no. 2, it follows that nearly 89% of iron ions are in  $\text{Fe}^{3+}$  and 11% in  $\text{Fe}^{5+}$  (or  $\text{Fe}^{4+}$ ) valence states at 4.2 K. The problem of  $\text{Fe}^{5+}$  or  $\text{Fe}^{4+}$  can be resolved starting from the charge-neutrality condition and the relatively stable oxidation state of  $\text{Co}^{3+}$  [6]. The oxygen content in sample nos. 2 and 3 is  $\sim 2.9$  atoms per formula unit. At this value the calculated oxidation state of B-site ions should be 3.2+, i.e. 80%  $\text{Fe}^{3+}$  and 20%  $\text{Fe}^{4+}$  or 90%  $\text{Fe}^{3+}$  and 10%  $\text{Fe}^{5+}$ . The observed 11% content of the subspectrum with  $B = 29.4$  T undoubtedly shows that only the second case is realized in sample nos. 2 and 3. A similar nonequivalent mixed-valence state of iron,  $2\text{Fe}^{4+} \leftrightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ , has been observed in  $\text{LaSr}_2\text{FeO}_{8+y}$ ,  $0.1 < y < 0.6$  [7]. The measured Mössbauer data for the magnetic field at the  $\text{Fe}^{3+}$  nucleus in sample no. 1 (without Co) are consistent with a 0.8  $\text{Fe}^{3+} + 0.2 \text{Fe}^{4+}$  distribution of iron oxidation states. Profile analysis of low-temperature ND spectra of sample nos. 1, 2 and 3 shows that the best fit is obtained for a G-type antiferromagnetic (AF) ordering of B-site spins in a magnetic unit cell which coincides with the chemical one. Significant quadrupole splitting indicative of a distortion of  $\text{FeO}_6$  octahedra was observed only after thermal treatment at 850 K during 2 h in vacuum for the  $B = 26.6$  T component of sample no. 3. From the temperature dependence of the Mössbauer line width, sample no. 2, Fig. 3, a temperature of Fe-spin ordering,  $T_{\text{Fe}} = 154$  K, was found. At this temperature, the magnetic moment of B-site ions (0.5 Fe + 0.5 Co), determined by ND, reveals only a slight kink. ND data show another temperature of an AF transition of nearly 285 K. The observed phenomenon shows that in sample no. 2 there exist at least two types of magnetic structures with differing transition temperatures and only one type of long-range magnetic ordering. MS data show the existence of a magnetic transition of the  $\text{Fe}^{3+}$  spin arrangement in sample no. 2 at  $T_{\text{N}} = 154$  K, which does not affect the long-range magnetic order. After the thermal treatment, sample no. 3, both MS and ND data show an increase in the magnetic transition temperature. The tendency of substituted or oxygen-deficient perovskites to demonstrate microdomain behaviour



**Fig. 3.** Mössbauer line-width parameter  $\Gamma(T)$  and magnetic moment from ND as a function of  $T$ , sample no. 2

is underlined by many authors [8, 9]. They suggested the existence of spatial separation of Fe and Co ions occupying B-sites, thus forming Co- and Fe-rich regions. The observed experimental facts: the magnetic splitting of the Zeeman sextet; a well-defined (by MS) transition temperature for ordering of Fe spins; absence of long-range order of Fe magnetic moments from ND data and correlation between transition temperatures determined by MS and ND, sample no. 3, lead to the conclusion that the most probable explanation is the formation of small clusters of ordered Fe spins which do not show long-range magnetic order. The Co-enriched sample consists of antiferromagnetically ordered spins similarly to that observed in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.9}\text{Fe}_{0.1}\text{O}_3$  [10]. The magnetic structure of the studied compositions shows a high instability in relation to the temperature, probably due to the atomic redistribution and loss of oxygen. At high temperature (850 K) the oxygen content in each formula unit of sample no. 3 decreases from 2.92 to 2.84. The magnetic moment of sample nos. 2 and 3 remains practically the same,  $\mu_{\text{B-site}} = 1.64 \mu_{\text{B}}$  at 60 K, and the unit cell keeps its rhombohedral symmetry,  $R\bar{3}c$ .

### 3 Conclusion

Using neutron diffraction it was found that the parent cubic structure of the studied samples is compressed along the  $\langle 111 \rangle$  direction and the oxides possess a rhombohedrally distorted unit cell – space group  $R\bar{3}c$ . The oxidation of B-site  $3d$  elements in itself cannot compensate the charge imbalance introduced by bivalent alkaline-earth atoms replacing  $\text{La}^{3+}$  on  $(6b)$  positions. Both studied compositions are oxygen-deficient (2.84 to 2.92 oxygens per formula unit). By increasing the temperature the lattice deformation decreases and at 850 K a cubic symmetry was established. A magnetic G-type AF order was registered below room temperature in both compositions. Whereas in  $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{2.85}$  the parameters of the magnetic structure, especially the transition temperature, determined by MS and ND, coincide, in the mixed B-site composition the data differ significantly. The Fe-spin ordering registered by MS at 154 K does not affect the long-range order of the magnetic structure. The AF transition temperature determined by ND is  $T_N = 285$  K.

*Acknowledgements.* The authors are grateful for the financial support of the EC (Contract No. HPRI-CT-1999-00020) for the ND experiments carried out in BENSCH-HMI, Berlin.

### References

1. O. Yamamoto, Y. Takeda, R. Kanno, M. Noda: *Solid State Ionics* **22**, 241 (1987)
2. J. Rodríguez-Carvajal: FullProf Version 3.5d (CEA-CNRS LLB, Oct98)
3. M. Eibschütz, S. Shtrikman, D. Trevest: *Phys. Rev.* **156**(2), 562 (1967)
4. J. Linden, M. Lippma, P. Karen, A. Kjekshus, M. Karppinen: *J. Solid State Chem.* **138**, 87 (1998)
5. A. Awana, S. Dou, I. Felner, I. Nowik, S. Malik, A. Mehta, R. Singh, A. Narlikar, W. Yelon: *J. Appl. Phys.* **83**(11), 7312 (1998)
6. A. Petrov, O. Kononchuk, A. Andreev, V. Cherepanov, P. Kofstad: *Solid State Ionics* **80**, 189 (1995)
7. P.D. Battle, T.C. Gibb, S. Nixon: *J. Sol. State Chem.* **77**, 124 (1988)
8. V. Sathe, A. Pimpale, S. Roy: *J. Magn. Magn. Mater.* **189**, 346 (1998)
9. T. Gibb, M. Matsuo: *J. Solid State Chem.* **81**, 83 (1989)
10. R. Sonntag, S. Neov, V. Kozhukharov, D. Neov, J.E. ten Elshof: *Physica B* **241–243**, 393 (1998)