

Short communication

Hyperfine interactions in $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-d}$, $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y-z}\text{Fe}_y\text{Ni}_z\text{O}_{3-d}$ perovskites

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Abstract

The paper presents results of Mössbauer effect measurements performed at 300 K and 80 K on series of perovskite structured, ABO_3 type oxides of the $(\text{La-Sr})(\text{Co-Fe-Ni})\text{O}_3$ compositions. The nature of hyperfine interactions (i.e. of dominating electric quadruple or alternatively, magnetic split) within the B sublattice was found to be dependent on which sublattice (A or B) has diverse occupancy. Hyperfine magnetic interactions split the spectra at low temperatures, what enables to distinguish discrete valences of iron ions and show that in the $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ and $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-d}$ cathode materials there is a mixed-valence $\text{Fe}^{3+}/\text{Fe}^{5+}$ rather than $\text{Fe}^{3+}/\text{Fe}^{4+}$ as could be expected. The presence of the mixed valence $\text{Fe}^{3+}/\text{Fe}^{5+}$, what seems to be microscopic, electronic reason for high catalytic activity toward oxygen reduction, was attributed to charge disproportionation reaction $2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ caused by substitution of Fe^{3+} with Ni^{2+} ions. Spin–spin relaxation phenomena in magnetically ordered state of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-d}$ and $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ samples were observed and the appearance of the magnetic order was attributed to decrease of the relaxation rate of the magnetic moment of iron.

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1. Introduction

LFN, LSCF and LSCFN are commonly used abbreviations for large group of perovskite structured, ABO_3 type oxides of $\text{LnFe}_{1-x}\text{Ni}_x\text{O}_{3-d}$, $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_y\text{Fe}_{1-y}\text{O}_{3-d}$ and $\text{Ln}_{1-x}\text{Sr}_x\text{Co}_{1-y-z}\text{Fe}_y\text{Ni}_z\text{O}_{3-d}$ ($x \geq 0$; $y, z \leq 1$; where Ln = La, Sm, Nd, Gd, Dy) compositions, respectively. These materials are considered to be promising for application as cathode materials in solid oxide fuel cells operating in so called intermediate temperature range (IT-SOFC) [1–3]. The demanded drop in SOFC operation temperature (down to $\sim 600^\circ\text{C}$) is driven by thus obtained reduced high temperature corrosion and chemical degradation of used materials. Moreover, this enables usage of cheaper and more environment friendly materials and creates fewer problems with a cell stack sealing. On the other hand, the lower operating temperature has serious drawbacks: slower oxygen diffusion and lower catalytic activity of a cathode as well as lower electrical conductivity of a solid electrolyte and

electrode materials. The strategic goal of numerous studies that are presently undertaken, is to find out microscopic factors that determine (and then to tailor them) mutually correlated properties of the materials, such as catalytic activity towards breaking the covalent bond of the O_2 oxidant molecule, electronic and ionic transport properties, thermal expansion coefficient and chemical stability, by choice of their optimal chemical composition, as well as preparation method. It is worth noting, that although many transition metal oxides are metallic, there are only few of them that are also good oxide-ion conductors in the oxidizing atmosphere that is present at the cathode side of an IT-SOFC. In case of the LSCFN compounds the more strontium replacing lanthanum the more oxygen vacancies are created, what improves their ionic conductivity [4]. Moreover the oxygen vacancies are usually accepted to be catalytic active sites for oxygen reduction [5].

In this study local interactions within the B sublattice of LFN, LSCF and LSCFN group of perovskite structured samples of $\text{LaFe}_{1-x}\text{Ni}_x\text{O}_{3-d}$ ($x = 0.2, 0.3, 0.4$), $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ and $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y-z}\text{Fe}_y\text{Ni}_z\text{O}_{3-d}$ ($x = 0.1, 0.2, 0.3$; $y = 0.4$; $z = 0.1, 0.2$) were studied by means of transmission ^{57}Fe Mössbauer spectroscopy performed at 300 K and 80 K.

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2. Experimental

LFN, LSCF and LSCFN perovskites were synthesized using precursors obtained by the modified citric acid method [6]. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in water. Solutions were heated in air up to 400°C . Obtained precursors were milled in a mortar, pressed into pellets and heated in air at 600°C , crushed in mortar again, formed into pellets and heated in pure oxygen atmosphere at 750°C . The final heating was performed at a temperature within the $1000\text{--}1200^\circ\text{C}$ range, depending on the sample chemical composition. Mössbauer effect measurements were performed at 300 K with a spectrometer working in constant acceleration mode in transmission geometry with the $^{57}\text{Co}(\text{Cr})$ source. The indicated values of isomer shift are relative to the source. Measurements at 80 K were done with Oxford Instruments bath type cryostat.

3. Results and discussion

Fig. 1 presents the surrounding of the B site in the perovskite structure of ABO_3 compounds. In the first coordination sphere of the B site there are eight rare earth ions from the A sublattice, while the six transition metal ions are the next-nearest neighbours. The B site symmetry and occupation of the neighbouring positions determines to some extent the nature of hyperfine interactions. In case of the LSCFN compounds where the A site is randomly occupied with La or Sr ions the quadruple splitting of Mössbauer spectra is apparent, however, the lower is the Sr content the greater is the determined electric field gradient (Fig. 2). This can be easily explained by progressing increase of charge symmetry of the B site with increasing Sr content, what is seen as practical absence of the quadruple split in case of the $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ sample (Fig. 4) likewise at 300 and 80 K. For the LFN series the unique occupation of the A site by La ions results in absence of quadruple splitting,

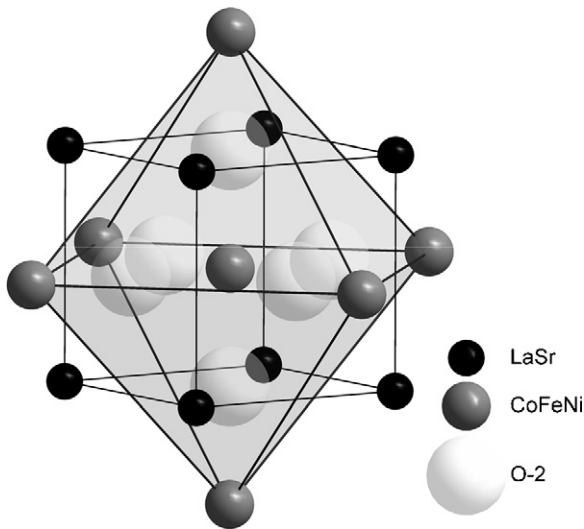


Fig. 1. The first and the second coordination sphere of the B site in the perovskite structure of ABO_3 compounds: the eight nearest neighbour rare earth ions and the six next-nearest neighbouring 3d ions.

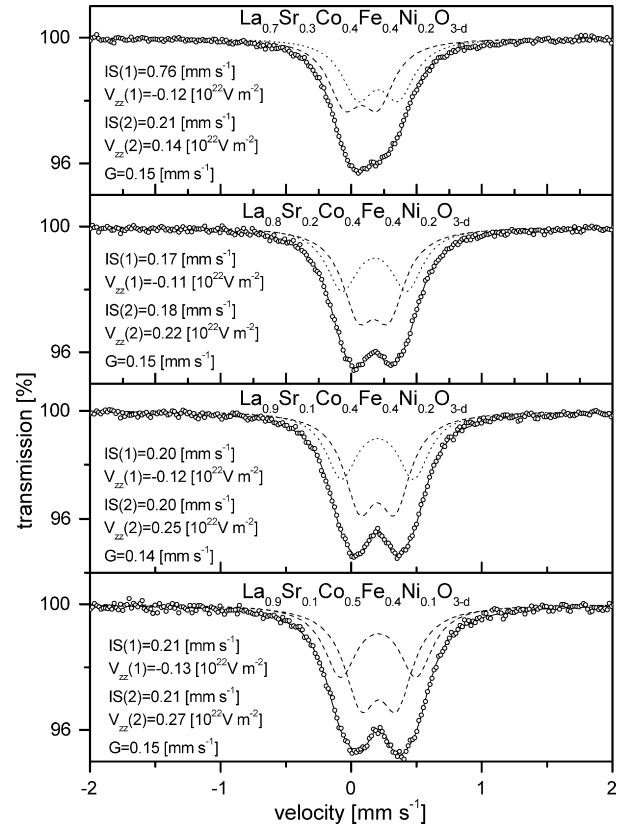


Fig. 2. Mössbauer spectra of series of LSCFN compounds at room temperature ($T = 300\text{ K}$). The solid line is the sum of the fitted components shown as dashed lines.

irrespective of the paramagnetic or magnetically split character of the spectrum (Fig. 3). The Mössbauer spectra recorded for the samples with Fe substituted with Ni exhibit features of complex magnetic hyperfine structure. For increasing substitution degree of iron atoms with nickel a progressive transition from a magnetically ordered state to that of a spin-disordered state was observed. In the spectra a distinct and similar broadening of external lines of each sextet was observed owing to spin–spin relaxation phenomena what seems to be responsible for the disappearance of the magnetic split of the spectra at RT (the relaxation becomes faster than the characteristic Mössbauer experiment time window). Similarly the increase in the oxygen vacancy concentration was also reported to depress the transition temperature between paramagnetic and magnetically ordered state and to cause a degree of relaxational collapse in the magnetic hyperfine pattern. The behaviour of iron magnetic moments reflects the process of freezing of iron spins relaxation and points to formation of a spin-glass phase as a result of disordered doping with magnetic Ni ions [7]. Slowing down of relaxation of iron spins with increasing Fe content in the LFN series suggests that the Fe–Ni magnetic exchange interaction is weaker than those of Fe–Fe pairs. The reference material for the LFN series is LaFeO_3 , where one magnetic sextet is necessary to fit the Mössbauer absorption pattern, originating from single valence state of iron (Fe^{3+}) occupying a unique crystallographic site. The magnetic properties of the LaFeO_3 (for which huge $B_{\text{hyp}} = 52\text{ T}$ were found) point to presence of high-spin ($S = 5/2$) $\text{Fe}^{3+} t_2^3 e^2$

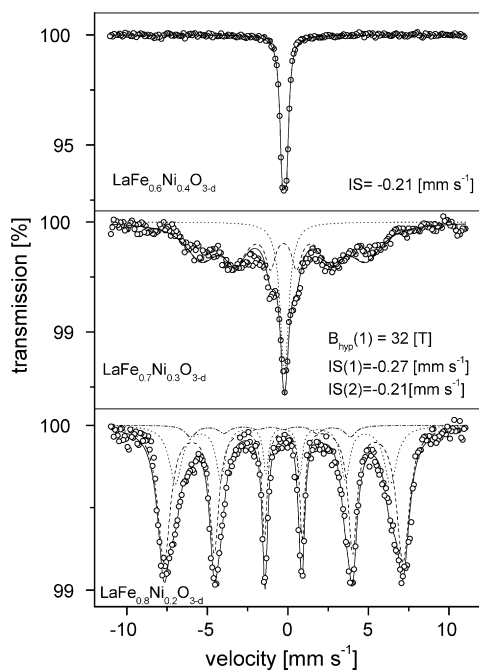


Fig. 3. Mössbauer spectra of the LFN series ($T=300\text{ K}$). For the $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-d}$ sample the determined hyperfine parameters are as follows: $B_{\text{hyp}}(1)=46\text{ T}$; $\text{IS}(1)=-0.27\text{ mm s}^{-1}$; $B_{\text{hyp}}(2)=41\text{ T}$; $\text{IS}(2)=-0.30\text{ mm s}^{-1}$; $B_{\text{hyp}}(3)=31\text{ T}$; $\text{IS}(3)=-0.10\text{ mm s}^{-1}$. The solid line is the sum of the fitted components (dashed lines).

electronic ground state of iron [8]. Evaluating the LFN spectra (Fig. 3) for each of the “magnetic” components the value of quadruple splitting (QS) was fixed to zero due to high symmetry of the B site, because when the QS was fitted, the obtained value was close to zero within determined numerical error range. For the substituted sample $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-d}$, it was necessary to fit the obtained spectrum with two magnetic sextets of slightly different isomer shifts (IS) and hyperfine magnetic fields (B_{hyp}) indicating presence of Fe^{3+} ions with different surroundings. This originates from nickel and iron random distribution over six next-nearest neighbour sites of an iron ion. However to obtain an acceptable fit of this spectrum it was necessary to assume a minor contribution ($\sim 5\%$) of component of remarkably different magnetic field ($B_{\text{hyp}3}=31\text{ T}$) and isomer shift (-0.10 mm s^{-1}). This component has been attributed to the coexistence of a different charge states within crystallographically equivalent Fe sites and supposed to represent high-spin Fe^{5+} , as the value of hyperfine magnetic field points to high-spin ($S=3/2$) state of Fe^{5+} . Assuming that for high-spin ($5/2$) Fe^{3+} the $B_{\text{hyp}}=52\text{ T}$, then the ratio $(3/2:5/2)52\text{ T}=31.2\text{ T}$, what nicely matches the determined value of $B_{\text{hyp}3}$. Moreover, the isomer shift of the component is equal -0.10 mm s^{-1} (-0.24 versus $\alpha\text{-Fe}$), what unambiguously points to the occurrence of Fe^{5+} in the sample. The absence of QS for all components is also consistent with the fact that the electronic configurations of both Fe^{3+} ($t_{2g}^3e_g^2$) and Fe^{5+} (t_{2g}^3) are highly symmetric. Furthermore, if Fe^{4+} ions would be present in high-spin states with localised electrons, the Jahn–Teller distortion should take place resulting in a distortion leading to electric quadruple splitting. The presence of Fe^{5+} can be attributed to charge disproportionation reaction of the type

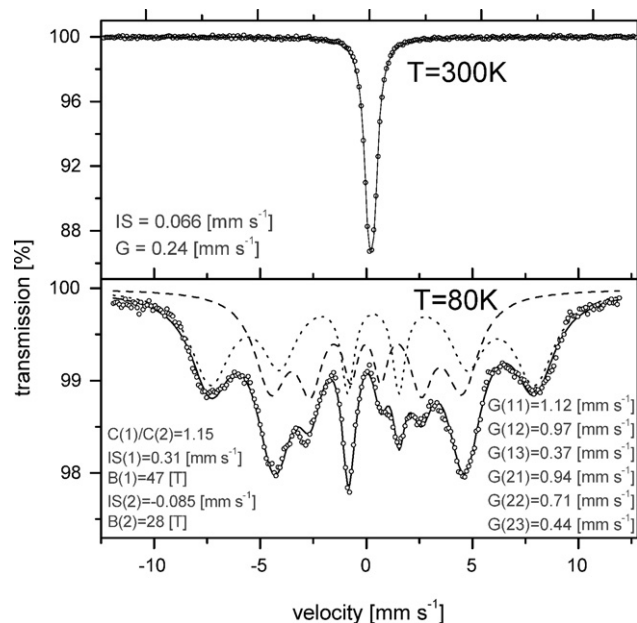


Fig. 4. Mössbauer spectra of the $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-d}$ sample measured at room temperature and $T=80\text{ K}$. The dashed lines represent fitted components while the solid one their sum.

$2\text{Fe}^{4+} \rightarrow \text{Fe}^{3+} + \text{Fe}^{5+}$ induced by substitution of iron by lower valence (Ni^{2+}) ions. The occurrence of the reaction seems to be related to observed higher catalytic activity toward breaking the covalent bond of the O_2 molecule of the nickel containing materials. In these systems there is a tendency for electron loose and this seems to be the microscopic, electronic reason for their catalytic activity toward oxygen reduction.

In case of the LSCF sample (Fig. 4) at RT the Mössbauer spectrum consists only of a single, slightly broadened absorption line, while spectrum taken at 80 K shows complex hyperfine interaction pattern. Surprisingly it was possible to fit this spectrum with only two “magnetic” components, exhibiting two distinctly different hyperfine magnetic fields (28 T and 47 T) with relative contributions 1:1.15 to the spectrum. Analogously, as in the previous case, assuming that here for high-spin ($5/2$) Fe^{3+} the $B_{\text{hyp}}=47\text{ T}$, the ratio $(3/2:5/2)47\text{ T}=28.2\text{ T}$ well matches the determined value of the lower hyperfine field pointing to occurrence of Fe^{5+} in the material. Therefore, the outer component of the spectrum was ascribed to Fe^{3+} ions in the octahedral sites and the inner one to Fe^{5+} ions in the octahedral sites. This is a mixed-valence state produced by the charge disproportionation into species approximating to Fe^{3+} and Fe^{5+} . However, while in the case of $\text{LaFe}_{0.8}\text{Ni}_{0.2}\text{O}_3$ sample the component originating from Fe^{5+} was a minor contribution, for the LSCF sample almost half of the iron atoms are in the high oxidation state developing due to the charge disproportionation reaction. Nevertheless this is not unexpected as it was shown already, that in the perovskite structure Co is more resistant to oxidation from the trivalent state than Fe [9]. Detailed inspection of the data given in Fig. 4 reveals also remarkable and coherent line broadening within each sextet. The range of the line broadening and progress of the broadening from inner to outer lines seem to originate in spin–spin relaxation phenomena (estimated relaxation

time is $\tau \sim 5 \times 10^{-8}$ s) rather than in hyperfine field distribution as it was suggested previously [10].

4. Conclusions

Mössbauer effect measurements performed on the series of iron containing LFN, LSCF and LSCFN perovskite structured, ABO_3 type oxides provide important information on the nature of hyperfine interactions within the B sublattice and make observable discrete valences of iron ions, while chemical methods yield intermediate valence state of iron [11]. The presence of mixed valence state of iron Fe^{3+}/Fe^{5+} and fluctuations of hyperfine parameters due to fast hopping of electrons from one Fe ion to another were observed in magnetically ordered state of $LaFe_{0.8}Ni_{0.2}O_{3-d}$ and $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-d}$ samples. The appearance of the magnetic order should be attributed to decrease of the relaxation rate of the magnetic moment of iron cations with decreasing temperature owing to increasing magnetic clusters size or the progressing freezing of the glassy spin structure. These phenomena seem to be directly related with the intermediate valence state of iron observed in these compounds also by chemical methods [11] and their metallic-type conductivity. The Fe^{5+} ions appear due to charge disproportionation reaction $2Fe^{4+} \rightarrow Fe^{3+} + Fe^{5+}$ induced by substitution of Fe^{3+} by Ni^{2+} ions. The occurrence of the reaction seems to be related to observed higher catalytic activity toward breaking the covalent bond of the O_2 molecule of the nickel containing materials. This provides an idea for tailoring catalytic properties of a SOFC cathode material by selecting such a composition of ABO_3 compound, in which within the B sublattice there is an ion that is forced to accept an oxidation state which is avoided by the ion in

certain structure (here it is the Fe^{4+}). In such a compound there is a tendency for electron loose and this is the electronic reason for their high catalytic activity toward oxygen reduction when operating as cathode in a SOFC.

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