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Investigation of the SrFe$_{1-x}$Co$_x$O$_3$ (0 ≤ x ≤ 1) Cubic Perovskites Obtained by Electrochemical Oxidation

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Abstract. The transition-metal perovskites SrFe$_{1-x}$Co$_x$O$_3$ (0 ≤ x ≤ 1) are of a great interest because the high oxidation states of the transition-metal (Fe(IV), Co(IV)) can be stabilized. Moreover these compounds exhibit interesting magnetic properties. These oxygen stoichiometric phases have been prepared only under high oxygen pressures. A novel preparation method of these phases has been investigated using electrochemical oxidation of the SrFe$_{1-x}$Co$_x$O$_3$ brownmillerite-type compounds [1-3]. The starting materials and the phases obtained after electrochemical processing have been characterized by X-ray powder diffraction, chemical analysis and $^{57}$Fe Mössbauer spectroscopy. Finally, the magnetic and transport properties have been studied.

1- PREPARATION

The starting material SrFe$_{1-x}$Co$_x$O$_{2.5}$ has been obtained using a classical nitrate route after many thermal treatments[1-3]. The electrochemical oxidation was carried out using the electrochemical cell as described elsewhere [4]. The electrode potentials quoted in this paper are referred to the Hg/HgO reference electrode ($E_{ref}$ = 0.098 V/ESH). The auxiliary electrode was a platinum foil. The ceramic of the starting material was used as the working electrode. Experiments were performed in KOH electrolyte at 25°C in air. The best conditions for the electrochemical preparation of SrFe$_{1-x}$Co$_x$O$_3$ are reported in the following table:

<table>
<thead>
<tr>
<th>x</th>
<th>anodic polarization</th>
<th>time</th>
<th>weight of electrode</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>potentiostatic E = 400 mV</td>
<td>63 h</td>
<td>400 mg</td>
</tr>
<tr>
<td>0.50</td>
<td>intenstostatic I = 250 µA</td>
<td>216 h</td>
<td>267 mg</td>
</tr>
<tr>
<td>1</td>
<td>potentiostatic E = 500 mV</td>
<td>180 h</td>
<td>400 mg</td>
</tr>
</tbody>
</table>

The electrochemical oxygen intercalation into the oxide network can be described by the following overall reaction:

$$2 \text{SrFe}_{1-x}\text{Co}_x\text{O}_{2.5} + 2\text{OH}^- \rightarrow 2 \text{SrFe}_{1-x}\text{Co}_x\text{O}_3 + \text{H}_2\text{O} + 2e^-$$

2- SrFeO$_3$ STUDY

The X-ray diffraction pattern of the brownmillerite before electrochemical treatment could be indexed with orthorhombic (12mb) unit cell. The lattice parameters obtained from a least square refinement were a = 551.9 pm, b = 1554.0 pm and c = 566.2 pm. The orthorhombic unit cell parameters are related to the cubic subcell parameter $a_c$ by $a = a_c = \sqrt{2}a$, and $b = 4a$, in this condition $a_c = 393.0$ pm. Chemical analysis revealed the presence of 6% of Fe(IV) in the sample before electrochemical processing corresponding to SrFe$_{2.53}$, Mössbauer spectrum recorded at 293 K is reported Fig.1a. This spectrum comprises two superimposed magnetic patterns and a small shoulder in the center of spectrum which reveals the presence of 5% of Fe(IV) in agreement with the chemical analysis. The Mössbauer parameters of SrFe$_{2.53}$, the isomer shifts and hyperfine fields, were calculated to be 0.376 mm.s$^{-1}$ and 49.7 T for octahedral iron site and 0.189 mm.s$^{-1}$ and 41.1 T for the one tetrahedral respectively.

After anodic polarization, the chemical analysis showed that sample contains indeed 100% Fe(IV). The unit cell parameter $a = 384.5$ pm is in good agreement with previous data relative to SrFeO$_3$ [5]. The Mössbauer spectrum at 293 K of the sample after electrochemical treatment (Fig.1b) shows a single symmetrical line. The Mössbauer parameters isomer shift $\delta = 0.082$ mm.s$^{-1}$ and $\Gamma = 0.494$ mm.s$^{-1}$ are characteristic of the existence of only Fe(IV). The absence of quadrupole splitting $\Delta = 0$ accounts for the symmetrical environment of Fe(IV) (regular octahedra) in good agreement with crystallographic data.
3- SrCo$_{0.5}$Fe$_{0.5}$O$_3$ STUDY

The X-ray diffraction pattern of SrFe$_2$Co$_{0.5}$O$_2$$_5$ characterizes a brownmillerite-type compound with an orthorhombic symmetry. The unit cell parameters, $a = 562.1$ pm, $b = 1569.0$ pm, $c = 549.3$ pm well agree with those previously found by Battle et al. [6]. Fig. 2a shows the Mössbauer resonance spectrum at 293 K of the SrFe$_{0.5}$Co$_{0.5}$O$_2$$_5$. This spectrum is composed of two Zeeman patterns. The values of the chemical shift ($\delta_{\text{Fe}} = 0.438$ mm/s$^{-1}$, $\delta_{\text{Td}} = 0.264$ mm/s$^{-1}$) and hyperfine field ($H_{\text{Fe}} = 48.4$ T, $H_{\text{Td}} = 39.8$ T) imply that iron is exclusively located either in octahedral (Oh) or tetrahedral (Td) sites. In addition one can note the small broadening of all lines in both sextuplets (0.33$\pm$ 0.50 mm/s$^{-1}$) caused by the random distributions of Fe$^{2+}$ and Co$^{3+}$ cations over the Oh and Td sites.

After electrochemical oxidation the powdered final product shows a well crystallized material with the cubic perovskite-type structure and a lattice parameter $a = 383.7$ pm; it is somewhat smaller than the one previously found by Takeda et al. [7]. The magnetic properties of the oxidized compound characterize a ferrimagnetic behavior with Curie temperature $T_c = 325$ K. The thermal dependence of Mössbauer resonance spectra of SrFe$_{0.5}$Co$_{0.5}$O$_2$$_5$ was studied in the temperature range between 298 and 341 K. Between 298 and 319 K, the spectra show the coexistence of the magnetic and paramagnetic patterns. This behavior is quite typical of relaxation effects of super-paramagnetic-type below $T_c$. The Mössbauer spectroscopy shows that the magnetic pattern disappears at $T_c = 327$ K. Above 330 K, the spectra were fitted by a broad single line ($\Gamma = 0.37$ mm/s$^{-1}$).

The isomer shift determined at 341 K (Fig. 2b) ($\delta = 0.07$ mm/s$^{-1}$) is characteristic of the tetravalent iron in octahedral site.

4- SrCo$_3$ STUDY

The starting compound is characterized by brownmillerite type structure with the following parameters: $a = 547.6$ pm, $b = 1576.9$ pm, $c = 554.8$ pm. The chemical analysis of the starting material reveals the formulation SrCo$_2$$_5$.

After anodic polarization, the XRD pattern was indexed in the cubic symmetry ($a = 383.5$ pm). Chemical analysis confirmed that in such conditions the stoichiometric phase SrCo$_2$$_5$ was prepared.

The SrCo$_2$$_5$ phase exhibits a semiconducting behavior before oxidation. After electrochemical treatment, the SrCo$_3$ compound is metallic and its magnetic properties characterize a ferromagnetic comportment. The Curie temperature ($T_c = 280$ K) was determined by thermal evolution of the magnetic moment measured at $H = 2$ T.

References