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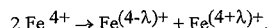
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Mössbauer Characteristics of the Nonstoichiometric $\text{Sr}_2\text{LaFe}_3\text{O}_{8+\delta}$ Perovskite Obtained by Electrochemical Oxidation

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Abstract. The nonstoichiometry and the vacancy ordering in the perovskite $\text{Ca}_2\text{LaFe}_3\text{O}_8$ has been investigated in previous works [1,2]. More recently, the occurrence of a large nonstoichiometric domain has been shown in the $\text{Sr}_2\text{LaFe}_3\text{O}_{8+\delta}$ system [3]. Thus, we have used a new "Chimie Douce" method: electrochemical oxidation which has been developed in our laboratory [4] for obtaining $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ in alkaline medium. The starting material $\text{Sr}_2\text{LaFe}_3\text{O}_8$ has been characterized by XRD, chemical analysis and Mössbauer spectroscopy. This compound contains only Fe^{3+} . The Mössbauer spectroscopy reveals, in the oxidized phase, the occurrence of antiferromagnetic interaction below $T_N = 195$ K with a good agreement with electric and magnetic measurements. At low temperature, the presence of two sextets can be explained in terms of a charge disproportionation:



1. INTRODUCTION

In this work, a new preparation method has been used to oxidize the G-type compound $\text{Sr}_2\text{LaFe}_3\text{O}_8$ (oxygen deficient perovskite): the electrochemical treatment. It is depicted as a novel and powerful route for preparing highly oxidized ferrites [1]. The reaction is achieved in alkaline solution, at room temperature, in air.

2. PREPARATION

For preparing the starting material $\text{Sr}_2\text{LaFe}_3\text{O}_8$, a stoichiometric mixture of SrCO_3 , La_2O_3 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is dissolved in nitric acid ($\text{HNO}_3:\text{H}_2\text{O}$, 1:1), then dried and slowly heated at 600-850°C for several hours. Pellets (\varnothing 8 mm, 2 mm thick, weight \approx 0.4 g) were pressed using an uniaxial pressure (2MPa, 2min) then sintered at 1250°C for 2 days and finally annealed at 1100°C for 10 h in Argon atmosphere; the temperature was then slowly decreased ($-50^\circ\text{C}\cdot\text{h}^{-1}$) to 900°C during 24 h in purified Ar before quenching. The compactness of the pellet prepared in this way was around 80%.

The electrochemical oxidation was carried out using an electrochemical cell with a three electrode device in NaOH, 1M solution in air. The reference electrode was a Hg/HgO electrode filled with 1M, NaOH ($E_{\text{ref}} = 0.098$ V/SHE, 25°C). All potentials quoted in this paper are referred to this electrode. The auxiliary electrode was a vitreous carbon foil. The ceramic of the starting material was used as the working electrode.

The electrochemical treatment can be described as an anodic polarization in potentiostatic conditions. The oxidation potential $E_{\text{ox}} = 500$ mV corresponding to the reaction : $\text{Sr}_2\text{LaFe}_3\text{O}_8 + 2\delta \text{OH}^- \rightarrow \text{Sr}_2\text{LaFe}_3\text{O}_{8+\delta} + \delta \text{H}_2\text{O} + 2\delta e^-$ has been determined from cyclic voltammetry studies. This anodic polarization was maintained during 8 days.

3. CHARACTERIZATION OF OXIDIZED MATERIAL

For the starting material, the XRD pattern shows a G-type compound with an orthorhombic symmetry. The unit cell parameters $a = 551.5$ pm, $b = 1189.6$ pm, $c = 560.6$ pm are in good agreement with those previously reported by Battle et al. [2]. After anodic polarization, powder XRD data gave a cubic perovskite unit cell with $a = 387.7$ pm.

The chemical analysis using Mohr salt titration revealed an increase of Fe^{4+} after anodic polarization. The composition of the starting material $\text{Sr}_2\text{LaFe}_3\text{O}_8$ became $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ after electrochemical oxidation treatment. It should be also noted that the decrease of the unit cell volume ($\Delta V/V \approx -4.9\%$) is due to the oxidation process.

The inverse magnetic susceptibility versus T for $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ is shown in Fig. 1. There is an abrupt change at about 190K with a minimum indicating a transition to antiferromagnetic ordering.

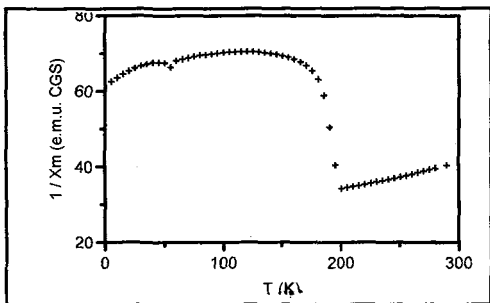


Fig. 1: Temperature dependence of reciprocal susceptibility for $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$

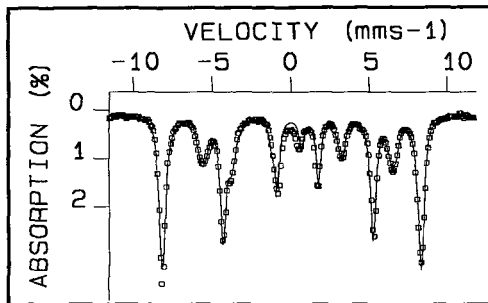


Fig. 2: Mössbauer spectrum at 293K of $\text{Sr}_2\text{LaFe}_3\text{O}_8$

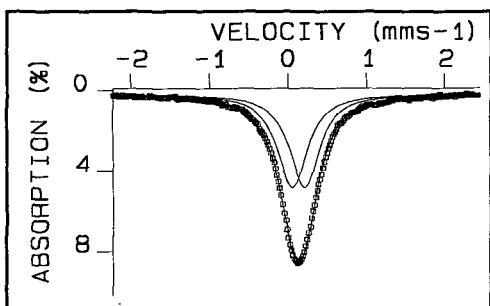


Fig. 3: Mössbauer spectrum at 293K of $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$

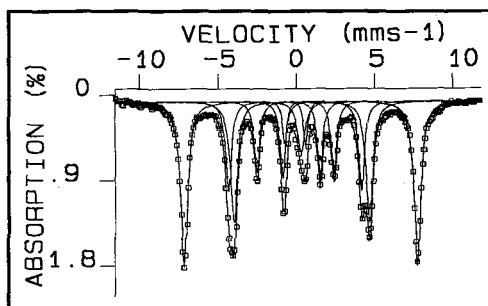


Fig. 4: Mössbauer spectrum at 4.2 K of $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$

4. MÖSSBAUER RESONANCE STUDY

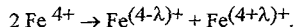
Figures 2 and 3 show the Mössbauer resonance spectra at 293 K of the $\text{Sr}_2\text{LaFe}_3\text{O}_8$ starting material (Fig. 2) and that of the final $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ compound (Fig. 3).

The Mössbauer resonance spectrum of the $\text{Sr}_2\text{LaFe}_3\text{O}_8$ starting compound (and its parameters) agrees well with the one reported by Battle et al. [5]. It is characteristic of the trivalent iron in octahedral (O_h) and tetrahedral (T_d) sites. The R ratio of iron in each site ($R = \text{Fe}(\text{O}_h)/\text{Fe}(\text{T}_d)$) has been obtained from the peak areas. This ratio is equal to that deduced from the structural model according to the ...OOTOOT... layer sequences as $\text{Ca}_2\text{LaFe}_3\text{O}_8$ compound [1,2].

The spectrum for $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ recorded at room temperature comprises a single symmetrical line. The lineshape is broad, the width of the peak is equal to 0.53 mm.s^{-1} and this spectrum can be fitted by a quadrupolar doublet with the characteristics: $\delta = 0.14 \text{ mm.s}^{-1}$; $\Delta = 0.16 \text{ mm.s}^{-1}$; $\Gamma = 0.35 \text{ mm.s}^{-1}$. The observed value for the isomer shift demonstrates the existence of a fast electron transfer and characterizes an "averaged" valence state for iron.

The thermal dependence of the Mössbauer resonance spectra of $\text{Sr}_2\text{LaFe}_3\text{O}_{8.90}$ was studied in the temperature range between 293 and 4.2 K. Between 293 and 200 K the spectra were constituted by only a quadrupolar doublet. Under 200 K, the spectra show the coexistence of magnetic and paramagnetic phases. This change agrees with the occurrence of the magnetic transition appearing below $T_N = 195 \text{ K}$.

At 4.2 K the spectrum comprises two superimposed magnetic hyperfine patterns (Fig. 4) with hyperfine fields of 46.6 and 26.4 T and isomer shifts of 0.36 and -0.03 mm.s^{-1} respectively. No quadrupole interactions on the subspectra are observed. The characteristics are consistent with a charge disproportionation:



These two magnetic hyperfine sextets, with area ratios of 70:30 are consistent with chemical analysis.

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