Fe(IV) Disproportionation in AFeO₃ (A = Ca, Sr) Perovskite Lattices Studied by 119Sn Diamagnetic Probe Mössbauer Spectroscopy

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Abstract. Fe(IV) is an interesting unusual oxidation state of iron stabilized under oxygen pressure. In a perovskite lattice such an oxidation state disproportionates into Fe(III) and Fe(V). The study of this phenomenon is important for a better knowledge of instable valencies. Using $^{119}$Sn as diamagnetic probe in the perovskite lattice of AFeO$_3$ (A=Ca,Sr) the disproportionation 2Fe(IV) $\rightarrow$ Fe(III) + Fe(V) is discussed versus local steric and electrostatic interactions.

1. INTRODUCTION

The formal Fe(IV) oxidation state has been stabilized in different oxygen lattices derived from perovskite or K$_2$NiF$_4$ structures using oxygen pressures [1]. In the $(AA')_2M_0.5$Fe(IV)$_0.5$O$_4$ (A=La, A'=Ca,Sr,Ba, M=Li,Mg,Zn) the high spin state ($t^3_2g^1z^2$) is mainly observed with a local Jahn-Teller distortion [2]. In the antiferromagnetic perovskite CaFeO$_3$, the disproportionation [2Fe(IV) $\rightarrow$ Fe(III) + Fe(V)] was detected at 280 K using $^{57}$Fe Mössbauer spectroscopy [3]. This phenomenon is not observed in SrFeO$_3$ characterized by a metallic behaviour [4] confirmed recently by theoretical calculations [5]. The purpose of this study was to evaluate in both oxides the role of the local electronic phenomenon on the Fe(IV) disproportionation. $^{119}$Sn was used as diamagnetic Mössbauer probe, the magnetic fields observed by $^{119}$Sn being dependent on the electronic configurations of neighbouring ions.

2. PREPARATION OF THE Sn-DOPED AFeO$_3$ PEROVSKITE (A=Ca,Sr)

These materials were prepared through a thermal treatment of a stoichiometric mixture of calcium or strontium nitrate (or carbonate) and iron hydroxide containing few amounts of Sn. In order to prevent strong modifications of the properties of the perovskite matrix, the doping level is small (0.5% at. Sn for CaFeO$_3$ and 1% at. Sn for SrFeO$_3$ enriched at 92% in $^{119}$Sn).

3. MÖSSBAUER INVESTIGATIONS

3.1 SrFeO$_3$ : 1% at. Sn

At 293K, two different absorptions are observed on the $^{57}$Fe Mössbauer spectrum attributed respectively to Fe(IV) (88%) - $\delta$(α-Fe) = 0.057 mm.s$^{-1}$, $\Gamma$=0.47 mm.s$^{-1}$ - and Fe(III) (12%) - $\delta$(α-Fe) = 0.27 mm.s$^{-1}$, $\Gamma$=0.30 mm.s$^{-1}$. The deduced stoichiometry is SrFeO$_{2.94}$. At the same temperature, the $^{119}$Sn spectrum corresponds to a singlet ($\delta$/CaSnO$_3$ = 0.11 mm.s$^{-1}$, $\Gamma$=0.88 mm.s$^{-1}$) characterizing Sn(IV) in oxides [6]. At 4.2 K, due to the antiferromagnetic ordering of SrFeO$_3$, the spin polarization of Sn(IV) induces a large diffuse absorption (Fig. 1) attributed to a large distribution of hyperfine fields. Such a distribution was analyzed through the Hesse and Rubartsch’s model considering a constant value for $\delta$ and $\Delta$ equal to 0 [7]. The resulting p(\text{H}) = f(\text{H}) diagram (Fig. 2) is symmetrical versus the average \text{H} value (220 kOe). This diagram was analyzed [9] in terms of a statistical distribution of Fe(III) ($t^3_2g^1e^2_8$) [Sn(\text{H}) = 270 kOe] [8] and Fe(V) ($t^3_2g^0$) [Sn(\text{H}) = 30 kOe for Cr(III)] [10].

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3.2 CaFeO$_3$ : 0.5% at.Sn

The $^{119}$Sn Mössbauer spectrum is given on figure 3. Using the same analysis than that developed for SrFeO$_3$: 1% at.Sn, a different hyperfine fields distribution is observed (Fig. 4) corresponding respectively to 6Fe(IV) and 5Fe(V) + 1Fe(III) in the near Sn surrounding [9]. Such a behaviour was attributed to steric effects inducing preferentially small cations in the first Sn(IV) coordination.

4. CONCLUSIONS

The use of Sn diamagnetic probe induces, in the SrFeO$_3$ lattice, the Fe(IV) disproportionation in the Sn vicinity due to a local slowing of the electronic delocalization. The Fe(III), Fe(V) distribution seems closely dependent on steric effects ($a_{\text{CaFeO}_3} < a_{\text{SrFeO}_3}$).

References