K$_2$NiF$_4$-type compounds are receiving considerable attention owing to their potential application as mixed conductors cathodes for solid oxide fuel cells at intermediate temperatures [1,2]. The crystal lattice of K$_2$NiF$_4$ structures can be described as a stacking of perovskite layers alternating with LaO rock salt layers [3]. These compounds have shown to exhibit a wide range of oxygen over-stoichiometry, which involves a considerable improvement of the transport properties [4]. This is due to their capability to accommodate interstitial oxygen in the LaO rock-salt layers. Besides, they present high catalytic activity for the oxygen reduction and an adequate thermal expansion coefficient that match with those of other cell components.

We performed X-ray absorption spectroscopy and X-ray diffraction of the samples La$_2$NiO$_{4+\delta}$, La$_2$CoO$_{4+\delta}$ phases and the related SrCo$_{(1-x)}$Sb$_x$O$_{3-\delta}$ perovskite oxides. First, we carried out the X-ray absorption spectroscopy (XAS); the wide energy range of the beamline makes it well-suited for XAS investigations on heavy elements with the possibility to access the K absorption edges for some elements. We determined the oxidation state of the Co cations in La$_2$CoO$_{4+\delta}$ and in SrCo$_{(1-x)}$Sb$_x$O$_{3-\delta}$ samples to obtain information about the oxygen contents in the species. First, we tried to normalize the XANES spectra. All the spectra were normalized respect to the value at ≈70 eV over the threshold and the references were CoO (Co^{2+}), SrCoO$_{2.5}$ (Co^{3+}), and BaCoO$_3$ (Co^{4+}). The Co K-edges of the series SrCo$_x$Sb$_{1-x}$O$_{3-\delta}$ are shifted to higher energies as the Co valence increases.

As one can observe in Fig. 1, all the edges of the SrCo$_x$Sb$_{1-x}$O$_{3-\delta}$ set indicate that the Co valences are between +3 and +4. As the Sb proportion increases, the oxidation state of Co evolves to higher values. Also, Sb introduces modifications in the XANES features, such as decrease of the pre-edge peak intensity at ≈7708 eV, or the increase of the so-called "white line" at ≈7724 eV.

Accounting for the linear relationship between the edge position and the oxidation state, the Co valence can be determined. Considering that the splitting of the 4p level (as one can see in the two shoulders of the SrCo$_x$Sb$_{1-x}$O$_{3-\delta}$ systems in the 1s→4p transitions, that is, the Co K-absorption edge), can impinge on the position of the maximum of the first derivative, the energy threshold has been estimated in all cases from the position of one third of the jump.

The average valence state of cobalt evolves from ≈+3.2 for the SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ to ≈+3.45 of SrCo$_{0.7}$Sb$_{0.3}$O$_{3-\delta}$. We can conclude that the evolution of the Co valence from 3+ to 4+ when the Sb content increases, is related to the increment of the oxygen content, being δ=0.71 for sample with x=0.95 and δ=0.085 for sample with x=0.7.
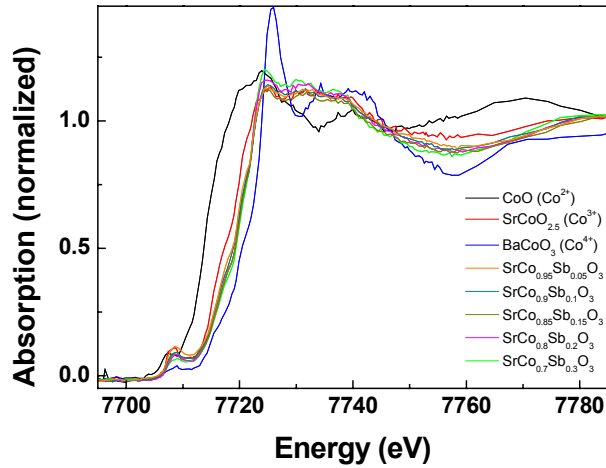
Fig 1: XAS spectrum of the series $SrCo_xSb_{1-x}O_{3-\delta}$

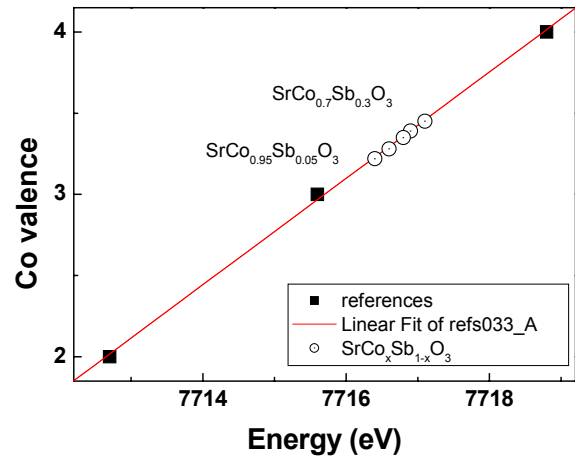Fig 2: Evolution of the Co valence state in the series $SrCo_xSb_{1-x}O_{3-\delta}$

1. E. Yvers-Yiffee, A. Weber, D. Herbstritt, J. Eur. Ceramic Soc., 21 (2001) 1505-1511.

2. H. Ullmann, N. T., F. Tietz , D. Stover , A. Ahmad-Khanlou, Solid State Ionics, 21 (2000) 79-90.

3. A. B. Stambouli, E. Traversa, Renewable and Sustainable Energy Reviews, 6 (2002) 433-455.

4. V. V. Kharton, A. P. Viskup, A. V. Kovalevsky, E. N. Naumovich, F. M. B. Marques, Solid State of Ionics, 143 (2001) 337-353.