Preparation of Mixed Oxygen-Ion and Electronic Conducting $Sr_4Fe_{6-x}Co_xO_{13}$ Thin Films by PLD

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In the last decade there has been an important activity in the research for new materials exhibiting mixed oxygen-ion and electronic conductivity for electrochemical applications, such as oxygen gas separation membranes, and cathode material in solid oxide fuel cells. Among those materials, $La_xSr_{1-x}Fe_yCo_{1-y}O_{3-\delta}$ perovskites have shown the highest conductivities (1). However, the wide variations of the oxygen nonstoichiometry makes them unstable at the working conditions of the final device, specially at the reducing atmosphere side in the case of gas separation membranes.

Some more complex mixed conducting oxides with perovskite-related intergrowth structures have been reported to show enhanced stability in a wide range of oxygen pressures, from pure oxygen to highly reducing atmospheres, while maintaining high values of their mixed conductivities. Such is the case of the Ruddlesden-Popper (R-P) series $(La,Sr)_{n+1}(Fe,Co)_nO_{3n+1}$ (n=1,2,3) and $Sr_4(Fe,Co)_6O_{13+\delta}$ (2). The structure of the $Sr_4Fe_{6-x}Co_xO_{13}$ material, which is the subject of this study, consists of an intergrowth along its *b*-axis of $Sr(Fe,Co)O_3$ perovskite blocks layers and $(Fe,Co)O_x$ layers. Recent studies reported the preparation of ceramic membranes with a composition $Sr_4Fe_4Co_2O_{13}$ (x=2), which showed high stability and a substantial oxygen permeability (3). However, those samples were proven to consist of a mixture of different phases (4,5), being the coexistence of the perovskite $Sr(Fe,Co)O_3$ the main responsible for the high oxygen permeability reported. Detailed experimental studies on ceramic samples have limited the stability of this structure to x≤1.8 (2). Moreover, in this compound, and induced by the layered structure, both electronic and oxygen-ion transport are expected to be anisotropic (4). The high crystal quality of epitaxial films would allow to study the intrinsic transport properties of this compound, as well as to minimize the effect of grain boundaries.

This study is, to our knowledge, the first attempt to grow epitaxial thin films of the $Sr_4Fe_{6-x}Co_xO_{13}$ compound. We have prepared two sets of films: $Sr_4Fe_6O_{13}$ (x=0) and $Sr_4Fe_4Co_2O_{13}$ (x=2), by pulsed laser deposition (PLD) on single crystal $SrTiO_3(100)$ substrates. For the $Sr_4Fe_6O_{13}$ we prepared sintered targets by solid state reaction from stoichiometric mixtures of $SrCO_3$ and Fe_2O_3 at 1150°C in air. For the Co-doped compound we used a commercial target with composition $Sr_4Fe_4Co_2O_{13}$. We used a Q-switched Nd:YAG laser with triple frequency (355 nm), 10 Hz repetition rate, and 2-3 J/cm^2 laser fluence, to deposit thin films at 10^{-1} mbar oxygen pressure, and different substrate temperatures, from 650 to 800°C. The Sr-Fe-O films prepared under different deposition conditions have shown to consist of $Sr_4Fe_6O_{13}$ phase with the long *b*-axis oriented perpendicular to the substrate surface. The effect of increasing substrate temperature favored the crystallization of $Sr_4Fe_6O_{13}$ phase, as shown in figure 1. However, it also induced the formation of epitaxial *c*-axis oriented $SrFe_{12}O_{19}$ phase, which has been already detected in the film deposited at 750°C, and becomes predominant at 800°C. The ϕ-scans of (271) $Sr_4Fe_6O_{13}$ reflection revealed a 4-fold symmetry in the in-plane alignment of the film. Figure 2 shows the surface morphology of the $Sr_4Fe_6O_{13}$ film, which shows a clear in-plane alignment of the film consisting of elongated crystals at 90° degrees. The optimum conditions for the growth of $Sr_4Fe_6O_{13}$ phase corresponded to 750°C substrate temperature, and 10^{-1} mbar oxygen pressure during the deposition process.

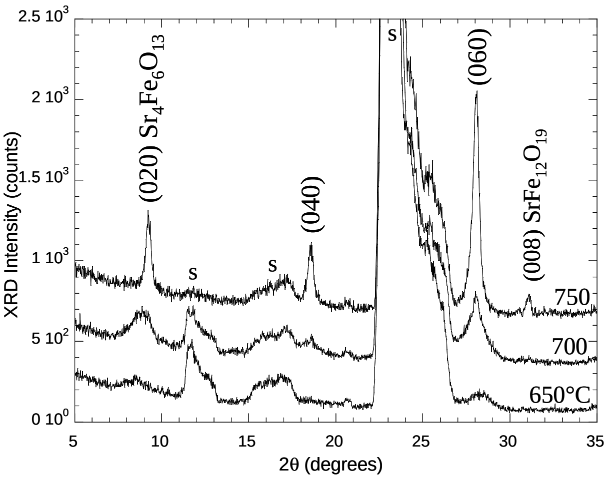

Fig.1. XRD patterns of Sr-Fe-O films on $SrTiO_3(100)$ substrates prepared at different temperatures which show increasing crystal quality of *b*-axis oriented $Sr_4Fe_6O_{13}$ phase.

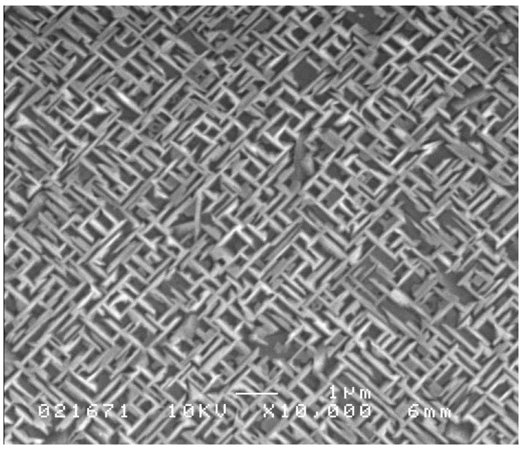

Fig.2. SEM image of the surface of the $Sr_4Fe_6O_{13}$ film grown on $SrTiO_3(100)$ substrate at 750°C

The same conditions were chosen as starting point to grow the $Sr_4Fe_4Co_2O_{13}$ films. In that case, the XRD patterns showed a combination of different phases. The peaks corresponding to the (*hh*0) $Sr_4Fe_{6-x}Co_xO_{13}$ reflections have been identified, in coexistence with other secondary phases such as (*h*00) $SrFe_{1-y}Co_yO_{3-\delta}$ perovskite, the (*h*00) $(Fe,Co)_3O_4$ spinel, and (Fe,Co)O and Fe_2O_3. Those results are in good agreement with the reported secondary phases obtained for this composition in bulk samples (5).

Further work is underway to optimize the conditions to obtain epitaxial $Sr_4Fe_{6-x}Co_xO_{13}$ film with different Co-doping within the solubility range, and to measure their transport properties.

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