Grain boundaries in strontium-doped lanthanum manganite thin films: the origin of mixed ionic-electronic conduction

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The large impact of grain boundaries (GB) on the electrochemical behaviour of polycrystalline oxides materials has received increasing attention in the last decades. While for a large number of oxides GBs have been demonstrated to be detrimental for oxygen mass transport properties, recent studies showed that they produces a large enhancement of oxygen diffusion in Sr-doped Lanthanum Manganite (LSM) polycrystalline thin films. To understand and control the extraordinary properties of LSM GBs, we deeply studied their chemical and structural composition in pulsed laser deposited polycrystalline thin films by High-resolution Transmission Electron Microscope (HR-TEM) and electron energy loss spectroscopy (EELS). The analysis revealed that a high density of dislocations occurs at the interface between the different grain orientations, along with a rearrangement of cationic composition. Also, the GBs show oxygen deficiency, which, in opposition with the typical hyper-stoichiometry presents in bulk LSM, appears to be the origin of the enhanced mass transport properties. We performed Density Functional Theory (DFT) calculation to investigate the formation energy of the cationic defects found in the GBs. The analysis revealed a strong intercorrelation among the various defects, helping to explain the local defect chemistry found by TEM. Finally, we analyzed the impact of the GBs local composition on electronic conduction, confronting polycrystalline and epitaxial thin films.