Mechanochemical synthesis, processing and printability of $La_{1-x}Sr_xTi_{1-y}Mn_yO_{3\pm\delta}$ perovskites as mixed ion-electron conducting (MIEC) materials

L. Zouridi[1,2*], E. Gagaoudakis[2], E. Mantsiou[2], A. Vourros[3], J. Garagounis[3], G.E. Marnellos[3,4], V. Binas[1,5**]

__1__ Department of Materials Science and Technology, University of Crete, Herakleion, Greece; __2__ Institute of Electronic Structure and Laser, Foundation for Research and Technology-Hellas; __3__ Chemical Process & Energy Resources Institute, Centre for Research & Technology Hellas, Thessaloniki, Greece; __4__ Department of Mechanical Engineering, University of Western Macedonia, Kozani, Greece; __5__ Department of Physics, University of Crete, Herakleion, Greece

Mixed ion-electron conductors (MIEC) have been studied in the past decades as electrodes for solid state electrochemical devices and as active materials for heterogeneous catalytic reactions, most notably in the high temperature regime (> 900^{o}C). Due to their high electronic and oxygen ion (O^{2-}) conductivity, MIEC metal oxides have been proposed and employed in a variety of applications including gas separation membranes, solid state batteries, solid oxide cell electrodes, and gas sensors. Perovskite metal oxide materials with a general formula of ABO_3 exhibit such conductive properties, with notable examples such as $SrTiO_3$. Additionally, in the field of solid oxide fuel cells and electrolysis cells (SOFC/SOEC) mixed oxide perovskite MIECs such as $LaMnO_3$ and Sr-doped derivatives have been extensively utilized as oxygen/air electrodes for the oxygen reduction reaction of molecular oxygen to oxide ion.

Conventional synthesis and deposition methods of such ceramic oxides for fabrication of solid state devices include sol-gel, solvothermal, and combustion synthesis, along with slot casting, screen-printing, chemical vapour deposition and electrodeposition, respectively. However, novel solvent-free synthetic routes of high yields, low toxicity and lower energy consumption, as well as contact-less direct deposition have been reported in recent years, in order to address scalability, cost reductions and sustainability of the manufacturing process.

In this work we present our most recent results on the solvent-free mechanochemical synthesis of a series of oxide perovskite ceramics, Sr-doped Lanthanum Manganates and Titanates with a general formula of $La_{1-x}Sr_xTi_{1-y}Mn_yO_{3\pm\delta}$ (with x, y = 0, 0.5 or 1), and their processing for ink formulation towards thin film deposition via inkjet printing. The structure and morphology of powdered materials have been physicochemically characterized (XRD, SEM, EDS). Additionally, powders were processed into colloidal inks in order to examine their printability by means of viscometry, particle size analysis (via DLS), surface tension characteristics and interfacial behaviour (via contact angle) on different substrates. Furthermore, deposition of synthesized materials as colloidal inks was achieved by inkjet printing, utilizing a Dimatix® Fujifilm printer, after the optimization of deposition parameters. For comparison, some conventional deposition techniques have been used, depending on the substrate (spin-coating, and/or screen-printing). The printed ceramic thin films were processed by thermal sintering and characterized physicochemically in order to define their structural and morphological properties. Finally, printed devices of MIEC perovskite ceramics were assessed for their applicability as electrodes in SOFC and gas sensing devices.

Acknowledgements This research was supported by "NSRF-EPAnEK" proposals "SMARTPACK" (T2EΔK-02373), "LIGBIO-GASOFC" (T1EΔK-01894) and "NANOLEFINS" (TAEΔK-06169).

---

*l.zouridi@iesl.forth.gr ** binasbill@iesl.forth.gr