Chemical routes for the synthesis at low temperatures of rare-earth scandate protonic conductors

Alessandra D'Epifanio, Patrizia Nunziante, and Enrico Traversa
Dipartimento di Scienze e Tecnologie Chimiche,
Università di Roma Tor Vergata
Via della Ricerca Scientifica, 00133 ROMA (Italy)

High temperature proton conducting oxides based on perovskite structure are currently investigated because of their potential use in several applications, such as separation membranes, solid state gas sensors, membrane reactors and electrolytes for fuel cells. H_2 separation membranes can find large application for hydrogenation-dehydrogenation processes in the petrochemical industry, for separation of hydrogen from fossil fuels and reformed natural gas. Compared to metal, polymer and microporous membranes, dense inorganic membranes offer new interesting chances in terms of high temperature operation, mechanical stability and selectivity.

Rare earth containing perovskites are promising materials as protonic conductors for such applications (1). In particular, protonic conductivity at high temperatures has been recently reported for rare earth scandates (2,3). The synthesis by solid-state reaction of rare earth scandates takes place at temperatures as high as 1400°C (3). In this paper, chemical routes that allow the synthesis of $LaScO_3$ and of $SmScO_3$ at temperatures as low as 600°C are reported.

Two preparation methods were used. The first synthesis was based on a polymeric precursor method (PPM): citric acid was used to chelate the cationic precursors, $La(NO_3)_3$ (or $Sm(NO_3)_3$) and $Sc(NO_3)_3$ (all Aldrich) by forming a polybasic acid. In the presence of a polyhydroxy alcohol, such as ethylene glycol, these chelates will react with the alcohol to form organic esters and water by-products. When the mixture is heated, polyesterification occurs in the liquid solution and results in a gel, in which metal ions are homogeneously distributed throughout the organic matrix. The solid resin is then heated up to high temperatures to get rid of organic residuals. The metal precursors are chemically combined to form the desired stoichiometric compounds during the pyrolysis process.

The second synthesis was a co-precipitation (CP). Stoichiometric quantities of $La(NO_3)_3$ (or $Sm(NO_3)_3$) and $Sc(NO_3)_3$ (all Aldrich) were dissolved in distilled water. Then, a 0.75 M solution of NaOH was added until to reach a pH of 8. At this value of pH a white colloidal precipitate is formed. After several washes with an alkaline solution (pH = 8) the samples were dried at 70°C. The samples obtained by this two techniques were annealed in air for two hours at selected temperatures in the range 500-1100°C.

The precursors were analyzed by simultaneous thermo-gravimetric-differential thermal analysis (TG/DTA). The calcined powders were characterized by X-Ray Diffraction (XRD) scanning electron microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS).

Figs. 1 and 2 show the TG/DTA curves for $LaScO_3$ prepared with the polymeric precursor and the co-precipitation methods, respectively. The TG curve shows that the weight loss is over at about 600°C for the powder prepared by PPM, while the weight loss is over at about 800°C for the CP powder. Moreover, an exothermic peak with its maximum at about 970°C is observed for the latter, attributable to a crystallisation or a solid-state reaction process. XRD analysis confirmed the presence of single-phase $LaScO_3$ when the PPM precursor was calcined at 600°C, while single-phase $LaScO_3$ was observed only after calcination at 1000°C of the CP precursor. After calcination at 900°C, peaks of other phases (single metal oxides) were observed, suggesting that a solid-state reaction occurred to complete the $LaScO_3$ formation. Similar results were observed also for $SmScO_3$. SEM observations showed that the chemical routes allowed to prepare powders with submicronic grain size.

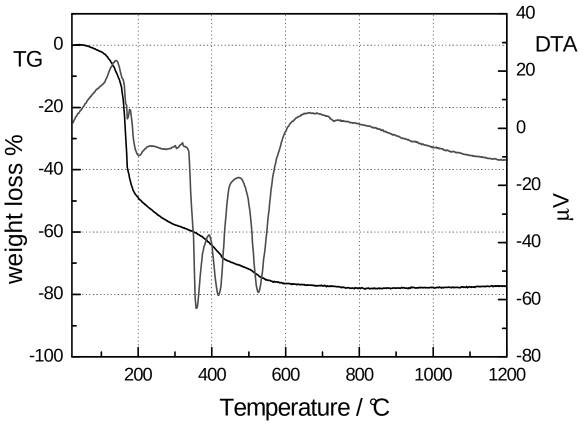

Fig. 1 – TG/DTA curves of $LaScO_3$ prepared by polymeric precursor method.

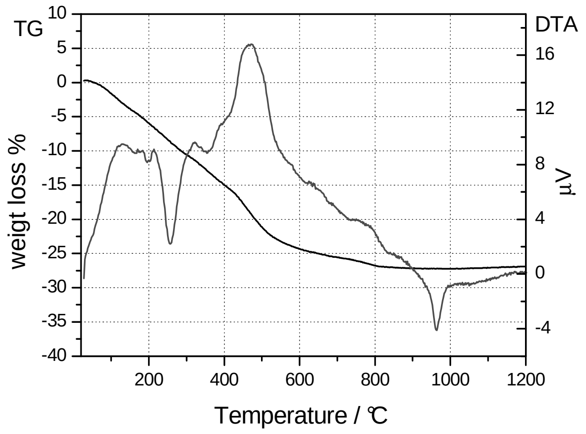

Fig. 2 – TG/DTA curves of $LaScO_3$ prepared by co-precipitation.

REFERENCES

(1) N. Imanaka and G. Adachi, *J. Alloys and Compounds*, **250**, 492-500 (1997).

(2) D. Lybye and N. Bonanos, *Solid State Ionics*, **125**, 339-344 (1999).

(3) H. Fujii, Y. Katayama, T. Shimura, and H. Iwahara, *J. Electroceram.*, **2**, 119-125 (1998).